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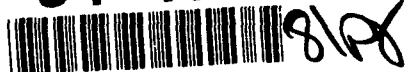
Heavy Metal Soil Contamination at U.S. Army Installations: Proposed Research and Strategy for Technology Development

by *R. Mark Bricka, Clint W. Williford, Larry W. Jones*
Environmental Laboratory

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Prepared for Headquarters, U.S. Army Corps of Engineers

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by **R. Mark Bricka, Clint W. Williford, Larry W. Jones**
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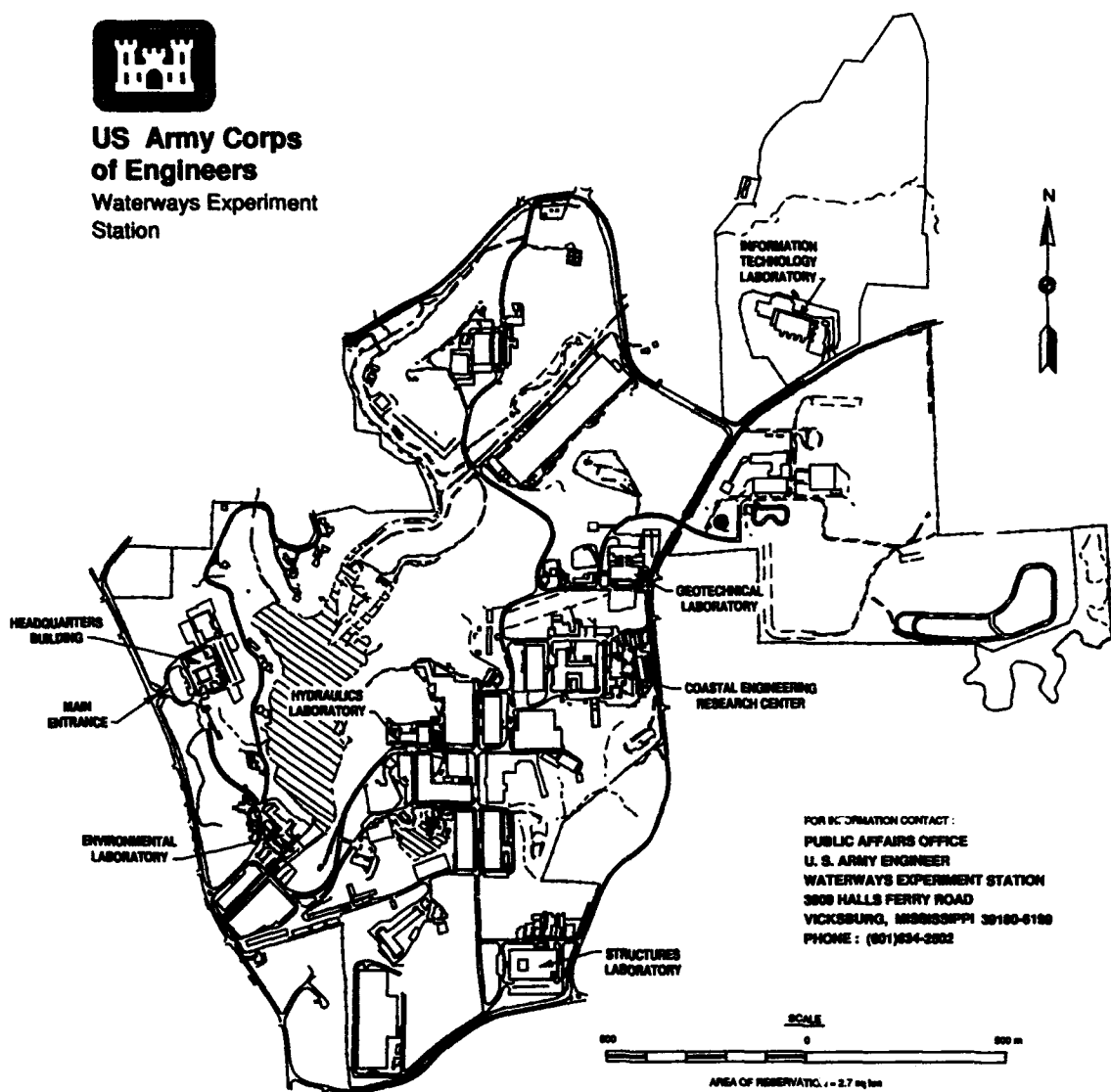
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Waterways Experiment
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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) as part of the Installation Restoration Research Program (IRRP) and the U.S. Army Environmental Quality Technology Research Program. This report is an extension of earlier work prepared by Roy F. Weston, Inc., performed under Contract No. DAAK 11-85-D0007 for the U.S. Army Environmental Center.

Dr. Clem Meyer was the IRRP Coordinator at the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers (HQUSACE). Dr. Bob York of the U.S. Army Environmental Center and Mr. Jim Baliff of the Environmental Restoration Division, Directorate of Military Programs, HQUSACE, served as the IRRP Overview Committee. Dr. John Cullinane, WES, was the IRRP Program Manager.

The work was performed during the period June 1991 to May 1992 by Mr. R. Mark Bricka of the Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES, and Drs. Clint W. Williford and Larry W. Jones, under contract to the ERB. At the time of publication, Dr. Williford was employed by the Chemical Engineering Department, University of Mississippi, and Dr. Jones was employed by the Waste Management Research and Education Institute, University of Tennessee. Special assistance for this work was provided by Dr. Cullinane. This report was prepared by Mr. Bricka and Drs. Williford and Jones.

The work was conducted at WES under the direct supervision of Mr. Norman R. Francingues, Chief, ERB, and under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Bruce K. Howard, EN.

This report should be cited as follows:

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
feet	0.3048	meters
miles (statute)	1.609347	kilometers
square miles	2.589998	square kilometers

1 Introduction

Background

Past military and industrial activities have contaminated numerous U.S. Army installations with metals, solvents, and explosives. Federal law requires that the Department of Army establish and implement an Installation Restoration Program (IRP) to clean up installations contaminated with hazardous materials resulting from past Army-related operations. Early assessments of the IRP revealed the immense scope of the needed restoration effort. Many of the contaminants found at these sites were unique to military-related activities. To execute their responsibility, the installations need effective, efficient, and economical solutions to solve the military-unique problems created by the manufacturing, use, and disposal of hazardous and toxic materials.

Historically, the Army leads the research effort with regard to military-unique compounds found in surface water, soils, and groundwater. Through its excellent research facilities, broad experience, capabilities, and scientific expertise, the Army has been assigned the lead service for assessing the hazardous waste associated with site remediation. Research is being actively pursued to establish cleanup criteria and to determine the effectiveness of current and new treatment technologies.

The U.S. Army Corps of Engineers (USACE) Research Directorate, through the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS, is responsible for executing research under the Installation Restoration Functional Area of the USACE Environmental Quality Technology (EQT) Research and Development program. The focus of this research is to provide the Army with the ability to decontaminate or neutralize hazardous and toxic wastes at military sites. Results of the research conducted in the EQT program provide the Army with a capability to comply with regulations mandated by Federal, State, and local environmental and health laws, to reduce the costs of compliance, and the potential to convert contaminated areas to land for productive use.

Important in this effort is the WES findings that metals contamination at military sites is widespread. In fact, heavy metals make up five of the six

hazardous substances monitored most frequently at Army installations, and 60 of the 89 IRP installations listed on the National Priorities List (NPL) cite heavy metals as one of the major contaminant problems (U.S. Army 1992). Historically, the military has not considered that metal contamination poses a large contamination problem, but evidence indicates that much more emphasis needs to be placed on addressing metal contamination problems.

Unlike organic contaminants that can be destroyed (or mineralized) by bioremediation, chemical oxidation, or incineration, metal contaminants are permanent and immutable. Once a soil has become contaminated with metals, the metals remain a potential threat to the environment until they are removed or immobilized. "Dig and Haul" is used almost exclusively for the remediation of heavy metal-contaminated soil. Disposal costs for contaminated soil that is trucked to a Resource Conservation and Recovery Act (RCRA) landfill may range from \$500 to \$1000/cubic yard, after all costs are included. As landfill space becomes more limited, these costs will escalate.

Purpose and Scope

This study provides guidance for understanding and developing new and innovative technologies for the treatment of heavy metal-contaminated soils at military installations. It includes a literature review of the scientific background for understanding the nature of heavy metal soil contamination, an analysis of the extent of metal contamination at a number of military installations, and a survey of available and potential soil treatment technologies. Based upon the results of these inquiries, technologies having a high potential for effectiveness for treatment of metal-contaminated soils are evaluated and prioritized. Specific objectives of this study are as follows:

- a. To further determine the nature and extent of heavy metals contamination for a representative number of U.S. Army installations.
- b. To assess the most promising technologies for treating metals-contaminated soil.
- c. To identify research and development needs to accelerate field implementation of select technologies in a 5-year time frame.
- d. To determine the research efforts and priorities required to develop the technologies that will achieve the remediation of the contaminated sites.

Need for Effective Treatment Technologies

Several events have converged that give impetus to the need for more effective treatment of metals-contaminated soil. First, with the end of the Cold War, the projected reduction in military resources will lead to the return of

military sites for public use under Base Closure and Realignment (BRAC). Second, the U.S. Environmental Protection Agency (USEPA) continues to strengthen regulations and enforcement regarding soil and water contamination. The national capacity variances that have allowed more flexible disposal of metals-contaminated soil and debris expired on May 8, 1992 (McCoy and Associates 1992). Also, it is expected that the Clean Water Act will be strengthened in the near future by lowering the amount of metals that may be contained in surface, drinking, and groundwater and still be considered safe. Third, growing public awareness of metals toxicity in soil and water will both force increased treatment and complicate disposal options. At least one major suit involving infant lead poisoning has been filed against installation administrators.

Three recent regulatory actions that will significantly impact action levels, treatment standards, and disposal activities are as follows:

- a. In October 1991 (USEPA 1991), the USEPA gave advance notice of proposed rules for "land disposal and restoration for newly listed wastes and contaminated soil." Treatment levels were to be specified in the proposed rules scheduled to be released in 1992 or 1993.
- b. In January 1991, the USEPA published proposed rules for debris treatment and disposal (McCoy and Associates 1992). These rules specify treatment methods and treatment limits for metals-contaminated debris.
- c. On May 1, 1992, USEPA issued a proposed Hazardous Waste Identification Rule. This would set concentration-based standards to allow treated RCRA waste (including contaminated soil) to be exempted from the RCRA system.

Finally, a number of proposed rule changes have been made in conjunction with the proposed debris rules that may also have bearing on the treatment and disposal of metals-contaminated soil (McCoy and Associates 1992).

- a. Debris may be excluded if it is treated by a specified technology and does not exhibit hazardous characteristics. Treatment using an immobilization technology would not qualify a waste for the exclusion.
- b. USEPA has proposed modifying the "indoor waste pile" restrictions to specifically exclude containment buildings used for the short-term storage and treatment of hazardous wastes. The proposed rules would be similar to those for tanks and containers. Generators would be allowed to accumulate wastes for up to 90 days without a permit. Also, the proposed rules set a number of standards for construction and operation, e.g., maintenance of negative pressure.

- c. Regarding the expiration of the national capacity variances, USEPA believes that sufficient treatment capacity can be developed in a short time. Permitted facilities may apply for authorization to add capacity under Class 2 or 3 and proceed with modifications while the permits are being reviewed.
- d. USEPA is seeking to encourage the recovery of metals as a "Best Demonstrated Available Technology" through use of high temperature metals recovery (HTMR). USEPA has proposed treatment limits for several heavy metals-contaminated wastes as illustrated in Table 1 (McCoy and Associates 1992). The waste specific residues from the thermal treatment could be disposed in a Subtitle D landfill if they met specified toxicity characteristic leaching procedure (TCLP) limits, given in Tables 2 and 3 (McCoy and Associates 1992), and did not exhibit other hazardous characteristics. Tables 2 and 3 are examples of proposed TCLP limits for F006 and K062 wastes and offer insight into proposed rules that are expected to parallel those for soil.

Project Activities

This study extends an earlier one performed by Roy F. Weston, Inc., for the U.S. Army Environmental Center (USAEC) (formerly the U.S. Army Toxic and Hazardous Material Agency (USATHAMA)). This earlier effort included a survey of heavy metals contamination at six military sites, a discussion of USEPA technology assessment criteria, and a review and evaluation of 22 technologies.

In October 1990, WES assembled a multidisciplinary advisory panel to review and update the earlier effort. The purpose of the advisory panel was to identify technologies potentially effective for treating metal-contaminated soils for further development under a limited research and development (R&D) program. The panel consisted of representatives of WES, USAEC, U.S. Bureau of Mines, USEPA, and experts from Purdue University, the University of Alabama, and the University of Tennessee. A listing of the panel members is given in Appendix A.

The advisory panel sought to identify promising technologies for the treatment of heavy metal-contaminated soils and research needs necessary to field one or more of the promising technologies within 5 years. Discussion addressed four major topic areas: physical/chemical processes, thermal processes, immobilization/stabilization, and other processes. Each topic was discussed individually.

In June 1991, WES surveyed 24 installations regarding their heavy metal soil contamination. Three installations were visited, and soil samples were collected from two of the sites.

Table 1
Existing and Proposed Treatment Standards for F006 and K062 Nonwastewaters

Constituent	F006 Nonwastewaters ¹		K062 Nonwastewaters ²	
	Existing Standard mg/l ³	Proposed Alternative Standard, mg/l ⁴	Existing Standard mg/l ³	Proposed Alternative Standard, mg/l ⁴
Antimony	--	2.1	--	2.1
Arsenic	--	0.055	--	0.055
Barium	--	7.6	--	7.6
Beryllium	--	0.014	--	0.014
Cadmium	0.066	0.19	--	0.33
Chromium (total)	5.2	0.33	0.094	0.19
Lead	0.51	0.37	0.37	0.37
Mercury	--	0.009	--	0.009
Nickel	0.32	5.0	--	5.0
Selenium	--	0.16	--	0.16
Silver	0.072	0.3	--	0.30
Thallium	--	0.078	--	0.078
Vanadium	--	0.23	--	0.23
Zinc	--	5.3	--	5.3
Cyanides ⁵ (total)	590	1.8	--	--
Cyanides ⁵ (amenable)	30	--	--	--

¹ F006-Wastewater treatment sludges from electroplating operations.
² K062-Spent pickle liquor from steel finishing operations.
³ Existing standards for metals are based on stabilization and are expressed as concentrations in TCLP extract (mg/l) for a single grab sample.
⁴ Proposed alternative standards for metals are based on HTMR and are expressed as concentrations in TCLP extract (mg/l) for a composite sample.
⁵ Cyanide standards are based on total composition (mg/kg). Source: 57 FR 975-976.

Results of the compilation of the efforts of Weston, USAEC, the advisory panel, and WES were subsequently used to formulate a research strategy to develop technologies for treatment of heavy metals in soil.

Report Organization

This report presents information to characterize heavy metal contamination at Army installations and evaluates and prioritizes potential treatment technologies. Emphasis is placed on those technologies showing promise for being field-ready within 5 years. It also offers a recommended strategy for additional R&D to speed implementation of the most promising treatment methods. Discussion and results appear in five chapters:

Table 2
Proposed Generic Exclusion Levels for F006 Nonwastewater
HTMR¹ Residues

Constituent	Concentration in TCLP Extract, mg/l
Antimony	0.063
Arsenic	0.055
Barium	6.3
Beryllium	0.0063
Cadmium	0.032
Chromium (total)	0.33
Cyanide (total) (mg/kg)	1.8
Lead	0.095
Mercury	0.009
Nickel	0.63
Selenium	0.16
Silver	0.30
Thallium	0.013
Vanadium	0.23
Zinc	44.0

¹ High temperature metals recovery. Source: 57 FR 1013.

Table 3
Proposed Generic Exclusion Levels for K062 Nonwastewater
HTMR¹ Residues

Constituent	Concentration in TCLP Extract, mg/l
Antimony	0.063
Arsenic	0.055
Barium	6.3
Beryllium	0.0063
Cadmium	0.032
Chromium (total)	0.33
Lead	0.095
Mercury	0.009
Nickel	0.63
Selenium	0.16
Silver	0.30
Thallium	0.013
Vanadium	0.23
Zinc	44.0

¹ High temperature metals recovery. Source: 57 FR 1013.

- a. Chapter 1. Introduction—provides the following:**
 - (1) Background on the nature of the problem and the Army's response to heavy metals contamination at Army installations.**
 - (2) Need for effective metals-treatment technology.**
 - (3) Purpose, scope, and objectives of this study.**
 - (4) Report organization.**
- b. Chapter 2. Survey of Heavy Metal Contamination at Military Installations—presents the results of literature reviews, phone surveys, and site visits to Army installations.**
- c. Chapter 3. Metal Contamination of Soils—describes the association of heavy metals with soil and explains the method of action of the major classes of soil treatment technologies.**
- d. Chapter 4. Review and Assessment of Soil Cleanup Technologies—prioritizes technologies most appropriate for Army research and development activity.**
- e. Chapter 5. Research Strategy for Metal-Contaminated Soils—provides the following:**
 - (1) Description of proposed research activities and efforts based on the review and technology assessment.**
 - (2) Prioritized list of research projects, including the research objective and technical approach summarized for each project.**

2 Survey of Heavy Metal Contamination at Military Installations

Introduction

This survey is an assessment of the extent and severity of heavy metal contamination at Army installations. Information for the survey is taken from the following sources, which are summarized briefly in this section:

- a. The publication *Defense Environmental Restoration Program: Annual Report to Congress (1992)*.
- b. Search of the USAEC's Installation Restoration Data Management Information System (IRDMIS) database, which identifies site types and contaminants and their concentration ranges by installation.
- c. Telephone survey encompassing 24 installations.
- d. Compilation of detailed concentration data for heavy metal-contaminated media from six installations.
- e. Site visits to five installations.

Defense Environmental Restoration Program's 1992 Report to Congress

Defense Environmental Restoration Program: Annual Report to Congress (1992) provides an overview of the IRP. The number of sites and the status of investigation and remediation at each of them is summarized in the report. Of over 17,600 potentially contaminated sites identified by the Defense Environmental Restoration Program, more than 10,000 have been investigated to some extent. At least one-third have been found to be clean and do not present a

health or environmental hazard. However, over 4,000 have been confirmed to present hazards. About 6,000 sites have yet to be investigated.

Specific information is presented for NPL sites. Of the installations on the list, 60 out of 89 have problems with metals contamination. For FUDS on the NPL, 7 out of 10 have metals problems. Bases slated for closure present a particular concern since they must meet environmental standards before being returned to civilian or alternative uses.

Survey of Available Databases

The IRDMIS database at USAEC contains detailed information from a selected group of Army installations. It catalogs analytical information from all samples taken at various sites on military installations and records their geographical location and soil depth. IRDMIS was used in June 1991 to find the number of occurrences of each cataloged contaminant. Five of the six most frequently found hazardous substances in the database are heavy metals. The IRDMIS was also searched to identify installations, site types, and contaminant concentration ranges for contaminated soils at Army sites.

A second USAEC database, the Defense Environmental Restoration Program Management Information System (DERPMIS), was queried for information in six major contaminant categories. DERPMIS contains site information for active military installations and properties in 76 separate data elements, including site names and descriptions, contaminants, and IRP site phase status. The Army portion of DERPMIS currently contains over 10,000 sites at more than 1,200 installations, including active Army facilities, Army Reserve Centers, and National Guard properties. Of the over 1,200 Army installations with metal contamination, more than 920 require further action because of metal contamination.

WES Phone Survey

A telephone survey was conducted by WES of 24 military installations that reported metal contamination. Facilities surveyed included Army depots, ammunition plants, arsenals, proving grounds, a missile range, and five bases. WES personnel were asked to characterize soils contaminated with metals in terms of the following:

- a. Major contaminant species.
- b. Sources of contamination.
- c. Types and number of sites.
- d. Status of IRP assessment and/or remediation action at the sites.

e. Availability of documentation and soil samples analysis.

Appendix B provides contacts, addresses, and phone numbers used in the survey. Table 4 summarizes findings of the survey. WES ranked the problems according to a subjective and qualitative scale. The numbers of problem areas (26 at 24 installations) and their ranking appear as follows:

Rank	No. of Areas	Description
1	3	Major problem on massive scale
2	6	Very serious (extensive cleanup project) with remediation still required
3	7	Serious with remediation still required
4	5	Serious, but remediation well underway
5	5	Not serious or already remediated

Other observations are as follows:

- a.* There is a wide disparity in the status of assessment and remediation among facilities. Six facilities had conducted some significant remediation, and ten had assessed their problems. Five had conducted only limited site investigations.
- b.* Firing ranges have not been assessed to any great extent.
- c.* The presence of chromium, lead, and cadmium were cited as the most often accruing soil contaminants. Organic soil contamination is also frequently cited in conjunction with metals contamination.
- d.* High metals soil concentrations (100's to 1,000's mg/kg) were cited seven times.
- e.* Fifteen of the facilities surveyed have problems that will prove costly, difficult, or beyond current technology to remediate.

Table 4
Heavy Metal Contamination at Select Military Installations

Base Activity	Major Contaminants	Source	Type No. Sites	Assessment and Remediation	Evaluation and Ranking of Problem
Annisbn, AD	Groundwater TCE, DCE, methochloride, Cr, Cd Cr (2,500 to 3,000 ppm) TCE ____ unknown	Electroplating, mechanical work	Chemical sludge waste pit, 28 solid waste management units	Remediation in 1982 and 1983, remedial investigation (RI) in 1988, more RI in 1991, plan to add Cr treatment to water	3
Corpus Christi, AD	Cr, 6 to 600 ppm in top 6 in. of soil, drops to 0.1 to 0.01 ppm deeper	Aircraft rebuilding	Sludge pit from industrial waste water plant	Now sampling and planning sludge pit closure	5
Fort Bliss	Chromic acid		Chromic acid pit	Pit has been sealed	4
Fort Hood	Pb, Cr, Cd, motor oils, fuels	Equipment maintenance, battery acid disposal?, leaking tanks, firing ranges	Work area ground, limestone pit, firing ranges, tank and artillery ranges extensive	Not required yet to do RI, now working to obtain Part B Hazardous Waste permit	1 and 2
Fort McClellan	Pb	Open burning of ordnance, detonation, firing range, sewage sludge	Ordnance burning areas, firing ranges, (sewage sludge within limits)	Not assessed yet	2 and 3
Fort Monmouth	Pb, sewage sludge, some oil spills	Pistol ranges, wastewater treatment	Pistol ranges, landfilled area with sewage sludge	Assessed in 1980 with USAEC updated in 1988	3

(Sheet 1 of 5)

Note: AD = Army Depot. AAP = Army Ammunition Plant. PG = Proving Ground. SWMU = Solid Waste Management Unit. A table of factors for converting non-SI units of measurement to SI units is presented on page viii.

Table 4 (Continued)

Base Activity	Major Contaminants	Source	Type No. Sites	Assessment and Remediation	Evaluation and Ranking of Problem
Fort Stewart	Pb, unexploded ordnance, phosphorus, napalm	Equipment maintenance, small arms and artillery firing ranges	Firing ranges on large scale, landfill with groundwater testing	Permitted RCRA, GAEPP burn site, closed low disposal sites (no Hg, Pb probl), Indust. areas "fairly clean," firing ranges not assessed	1 and 4
Iowa Army Ammunition Plant	Lead (27,000 mg/kg max); Mercury (32 mg/kg max)	Detonator mfg. effluent	1 linear mile drainage ditch; soil contam. to 5-ft depth	Assessed and cleanup completed about fall 1990	5
Letterkenny, AD	Hex Cr, volatiles (also in groundwater)	Electroplating, equipment maintenance, wastewater treatment plant	5 Super Fund sites: 2 solvent disposal, 1 oil dump, oil industry trmnt lagoon, electroplating site, 8- by 20-ft pit with max TCLP Cr 2, 9 mg/l, Tot Cr 4,000 mg/hg @ 2 ft; 300 mg/hg @ 6 ft. Area one of many contam. areas	Now involved in RI RCRA closure plan in draft form	2
Lonestar, AAP	Cr, Hg, Ba, Cr (45 to 1122 ppm), Hg (0 to 215 ppm), Ba (22.1 to 420 ppm)	Demilitarization of explosives, contaminated wastewater	Demolition/burning grounds, wastepits, 10 areas reported on	Remedial investigation carried out	3
Newport, AAP	TNT	Explosive disposal	6 to 7 burning ground sites	Now under RI	Metals not found to be a problem at burning ground 5

(Sheet 2 of 5)

Table 4 (Continued)					
Base Activity	Major Contaminants	Source	Type No. Sites	Assessment and Remediation	Evaluation and Ranking of Problem
Picatinny Arsenal	Explosives, Hg (one area 10 to 70 ppm), Pb, As, Cu, TPH	Explosives disposal, shell burial, tetra used to be put into pits	Burning and burial grounds, 150 sites	RFI contract awarded, not started yet, pump and rt plant on line in 1 month for TCE, will check about 6 to 7 areas this year	Of 150 sites, most will not be a problem 2
Pine Bluff Arsenal	Pb and AS main contaminants (2,000 to 30,000 ppm) also Ba and some Hg	Munitions mfg, testing, and burning	About 20 sites originally, now 8	Remediation completed over last 10 years, encapsulated with slurry barrier and sealed on top	4
Radford, AAP	Pb (6 percent in localized area), As, organics possible, but not evaluated	Lead recovery facility, acid wastewater	80 sites, "Several" with Pb and As	Remediated waste lagoons, removed soil in one case, site investigation underway	4
Ravenna, AAP	Pb (about 900 ppm), Zn and Cu (1,000 ppm, 900 at 3 ft), Cr ore piles, Cd in burning grounds	Disposal of munitions and storage of Cr ore	Deactivation furnace, demolition areas, burning grounds (200 acres), Ferro-Cr contamination of ore pads and stream	Will soon finish closure plan, have checked groundwater for Cr (none) and will monitor stream for Ferro-Cr	4
Red River, AD	Cd and Cr (5 to 30 ppm), organics anticipated (pesticides)	Electroplating painting tanks	Seven problem sites	RFI and IRP underway, boring now, preliminary results soon, final report due 1992	3
Redstone Arsenal	As (Prob very high)	As based process for mustard gas production; also decontam wash solutions from bombs	Several As lagoons: now leveled; total of 176 areas; not sure of ones with heavy metals	Huntsville Div. did RFI boring; not pursuing investigation at this time because of danger	2
(Sheet 3 of 5)					

Table 4 (Continued)

Base Activity	Major Contaminants	Source	Type No. Sites	Assessment and Remediation	Evaluation and Ranking of Problem
Rocky Mt. Arsenal	As (1,000's ppm), Cd and Cr (10 to 1,000's ppm); Hg (10 to 100's ppm); smaller amounts Pb and Zn generally some organics; pesticides	Demilitarization, burning	178 sites; about 100 need to be addressed	RI done; intermediate response taken for organics; conducting FS; vitrification and fixation being considered; questions about fate of Hg	As is main problem driving metals recovery 2
Sacramento, AD	None known; pumping water to remove organics				5
Tobyhanna, AD	Cd, Cu, and Zn; some PCBs in soil; elevated Cd in water (11 ppb)	Electroplating and circuit board mfg.	1 area	2 yr ago had prob.; hvy metal sludge on ground; some Cd in soil; reached agreement with EPA; removed and backfilled; have NPDES permit	5
Tooele, AD	Cr, Cu, Ni, Pb (5 to 30 ppm); possible munitions residue from open detonation sites Mercury (8,600 ppm) max	Wheeled vehicle maintenance, munitions and propellants storage and destruction Instrument fluid spill	Area 60 by 40 ft; 3.5 ft in depth	Soil sampling for at least six locations. Assessed excavated, hauled to haz waste landfill, completed Dec. 1990	3
White Sands Missile Range	Hex Cr (3,000 ppm), Pb (1,000's), organics, meth chloride, TCE, Mercury (10 mg/hg), Barium (3,600 mg/hg), TPH (1,000's to 10,000 Mg/Hg)	Laser test facility, Cr agent in cooling system fluid	5- to 10-square mile area affected. SWMU's 5 of 18 investigated (most "small" in area); some Cr may be dispersed over several square miles	Req'd RCRA facility; now doing assessment; solid waste mgmt unit; 75 more SWMU's to be investigated; No cleanup taken yet	3

(Sheet 4 of 5)

Table 4 (Concluded)					
Base Activity	Major Contaminants	Source	Type No. Sites	Assessment and Remediation	Evaluation and Ranking of Problem
Yuma Proving Grounds	Depleted U ²³⁸ , Pb (7 ppm and 20 to 60 ppm), Cd, Cr, As (9 to 20 ppm)	Open detonation, and burning; 1 solid wst mgmt unit; depleted U ²³⁸	Detonation, burning sites; firing range for large caliber U ²³⁸ , small hill area?; overall firing range 500,000 acres with Pb and other projectile debris	Corps from Sacramento will sample burning pits down to 30 to 35 ft; Los Alamos has studied long-term effect of U ²³⁸ ; Yuma contracting with Idaho Nat'l labs for study of separation of DU (depleted uranium)	1

(Sheet 5 of 5)

Detailed Analysis of Six Army Installations

Metal-contaminated soils, sludges, and soil treatment residues at the U.S. Army installations were characterized based on a review of existing hard copy reports on soil metal contamination data for all the sites (Weston 1987). From this broad review, six sites with known metal-contaminated soils were selected by USAEC to represent anticipated metals-contaminated soil sites. Table 5 (Weston 1987) shows the range of metal concentrations in soils for the six selected sites. The data are for total metals only. There is little or no information on background or leaching characteristics.

In the absence of toxicity data (extraction procedure [EP] or TCLP), these total metals analyses can be used only as rough indications of metal toxicity hazard. However, by assuming that 100 percent of the metal content of the soil is extracted using the EP or TCLP toxicity procedures, a "worst case" EP toxicity equivalent may be estimated. The toxicity test procedures call for the total weight of solution to be adjusted, prior to analysis of the leachate for metals, so that the weight of liquid extract equals 20 times the weight of the original sample. Thus, if the total metal concentrations exceed 20 times the EP toxicity limits for the extract, the sample could exceed EP toxicity limits under worst case assumptions. This procedure provides a hypothetical guideline for assessing total metal concentration data for U.S. Army installations. Table 6 (Weston 1987) summarizes the number of samples taken at the six sites that could hypothetically exceed the EP toxicity limit.

The composition of two waste streams that could potentially receive similar treatment for metals, electroplating sludge, and paint-stripping sludge are given in Tables 7 and 8. The electroplating sludge contains extremely high metals concentrations, far in excess of that found in soils; and the paint-stripping sludges also differ from soil, particularly with regard to moisture, pH, and the presence of organic solvents. Differences between soil and sludge waste properties suggest that many technologies may work with one, but not the other. Given that the ultimate objective of this study is to develop technologies for metals-contaminated soil treatment, technologies applicable to soils will be emphasized over those solely applicable to sludges.

Based on these considerations, the following was concluded:

- a. Many installations have possible soil contamination problems based on total metals concentrations.
- b. Chrome, lead, and cadmium most often exceed the hypothetical limit of 20 times the toxicity limit.
- c. Limited data exists on mobility of metals in soils at these installations.

Table 5
Range of Metals Concentration in Soils for Six Army Sites (total metals, ppm)

Site	Cr		Hg		Pb		Cd		Ba		As		Se		Ag	
	Low	Hi	Low	Hi	Low	Hi	Low	Hi	Low	Hi	Low	Hi	Low	Hi	Low	Hi
Letterkenny, PA	14	777	—	—	8.6	4,940	5.2	308	35	2,300	5.7	12.8	—	—	—	—
TCAAP, ¹ MN	7	146	0.1	2	3	3,000	1.5	31.3	6	3,800	—	—	—	—	—	—
Anniston, AL	1.2	3,000	0.00	23	1.16	956	0.05	453	0.49	343	2	—	—	—	5.58	—
Riverbank, CA	11	1,109	—	—	15	138	—	—	—	—	8	70	—	7	—	—
Louisiana, LA	9	441	—	—	9	89	—	—	—	—	—	—	—	—	—	—
Tooele, UT	—	30	—	—	—	—	—	—	—	—	8	100	—	—	—	—

¹ Twin Cities Army Ammunition Plant, New Brighton, MN.

Table 6
Metals of Concern in Soils at Army Installations Exceeding Toxicity Limits¹

Metal	Samples Exceeding Hypothetical Limit ²
Cr	47
Pb	13
Cd	7
Hg	1
Ba	1
As	1

¹ Based on USAEC database for six sites selected for focused study. Source: Weston (1987).

² Assumes 100-percent transfer of metals from the soil to the extract based on TCLP toxicity test procedures.

Table 7
Typical Electroplating Sludge Composition

Representative Compound	Typical Waste Range ¹ dry weight, %	Army Waste ² dry weight, %
Cu(OH) ₂	0-15	7
Cr(OH) ₃	0-15	10
Ni(OH) ₂	0-60	7
Cd(OH) ₂	0-1.5	1
Zn(OH) ₂	0-30	7
Fe(OH) ₂	0-40	7
CaSO ₄	—	61
Overall % solids	15-35	—

¹ Source: Tidwell (1986).

² Source: Hepworth (1985) and Chesler (1982).

- d. Technologies developed for typical high-metal wastes, such as electroplating or paint-stripping sludges, may be completely inappropriate for lower metal levels typical of soil contamination.

Table 8 Example Paint Sludge Composition¹				
Compound	Water Wash Spray Booth Sludges	Alkaline Paint Stripper Sludges	Organic Paint Stripper Sludge	EP Toxicity Limits
EP Toxicity, mg/l				
As	ND	--	--	5.0
Ba	0.05	--	--	100
Cd	ND	--	--	1.0
Cr	1.7	--	--	5.0
Pb	0.047	--	--	5.0
Hg	ND	--	--	0.2
Se	ND	--	--	1.0
Ag	ND	--	--	5.0
Total metals, mg/kg				
Cr	--	120	1,200	--
Cd	--	67	130	--
Pb	--	6	400	--
pH	8.8	9.3	0.9	--
Solids, %	44.9	60.4	26.3	--
Specific gravity	1.26	1.4	1.4	--
COD, mg/l	12,000	180,000	340,000	--
Fuel value Btu/lb	3,125	64	4,931	--
¹ Source: Hallowell (1984).				

Site Visits

Over the years, WES personnel have had many opportunities to observe contaminated sites and remediation efforts at various military and civilian sites. At this time, WES personnel have visited five military installations to specifically address sites with heavy metal soil contamination. The sites selected were as follows: Fort Ord, CA; Rock Island Arsenal, IL; Rocky Mountain Arsenal, CO; White Sands Missile Range, NM; and Umatilla Army Depot, OR. Contaminated sites were visited and photographed, and discussions were held with site environmental personnel who described the history, nature, and extent of contamination at their installation. Soil samples were collected at four of the five sites.

Soil contamination resulting from lead-based painted facilities is an example of an unexpected, major heavy metal problem. Lead-based paint represents an acute and growing concern for U.S. Army organizations directly responsible for facility maintenance and personnel health. For example, the Engineering Directorate in Hawaii has been assembling information and contacts to address all aspects of the lead-based paint problem. This concern is

driven by a growing awareness of imminent health hazards to personnel, environmental and health regulations, and litigation.

Many major installations in operation since World War II (WWII) have thousands of family quarters, many with lead-based paint contamination in and around the structures. Lead abatement actions will generate large amounts of lead-contaminated debris requiring some form of controlled disposal. In addition, the soil around buildings which have been painted with lead-based paints may also be contaminated. A Boston survey of inner city housing indicated soil concentrations of 300 to 3,000 mg/kg for the majority of housing tested. Efficient treatment technologies for lead-contaminated media, either soil or debris, are important to successful remediation.

Rock Island Arsenal, Rock Island, Illinois

There has been military activity at Rock Island Arsenal (RIA) since about 1814. A large complex of 10 stone manufacturing buildings were built shortly after the Civil War, including Buildings 64, 66, and 68 (Figure 1). Several of the facilities and soil areas expected to be contaminated have been sites of industrial operations underway for over 100 years, beginning shortly after the Civil War. Several of these buildings are now used for office space. Currently, it is proposed that contaminated buildings are to be decontaminated and converted to other uses, preserving them as historical assets.

A wide spectrum of RIA munitions and weapons manufacture processes have lead to a diversity of metal contamination problems. Major potential sources of contamination include electroplating, metals finishing, painting, burning grounds, casing burial grounds, coal and ash storage areas, and old landfill sites. Primary attention is now focused on the electroplating facilities, ash and coal storage areas, and landfills by the Sylvan Slough (Figure 1).

The electroplating facilities, Buildings 64, 66, and 68, are currently inactive. As a result of past operations, an extensive dark discoloration built up on one side of Building 64 where exhausts from pickling tanks were vented. Building 64 also has a large bright yellow and green stain on the side of the facility, presumably chrome that has drained from overhead roof vents. Several soil samples were taken around Buildings 64 and 66 and the data for the bulk analysis are shown in Table 9. According to site personnel, soil samples were combined into a pile on a "hard lot."¹ While the contaminated soil was composited with other less contaminated soil, high levels of metals were still found (100 to 200 ppm) in the TCLP leachate samples. Individual analysis of the contaminated samples (while not presented here) indicated the soil contained extremely high metal concentration ranging up to 100,000 mg/kg.

¹ Personal Communication, March 1992, Thomsa Gizicki, Environmental Coordinator, Rock Island Arsenal, IL.

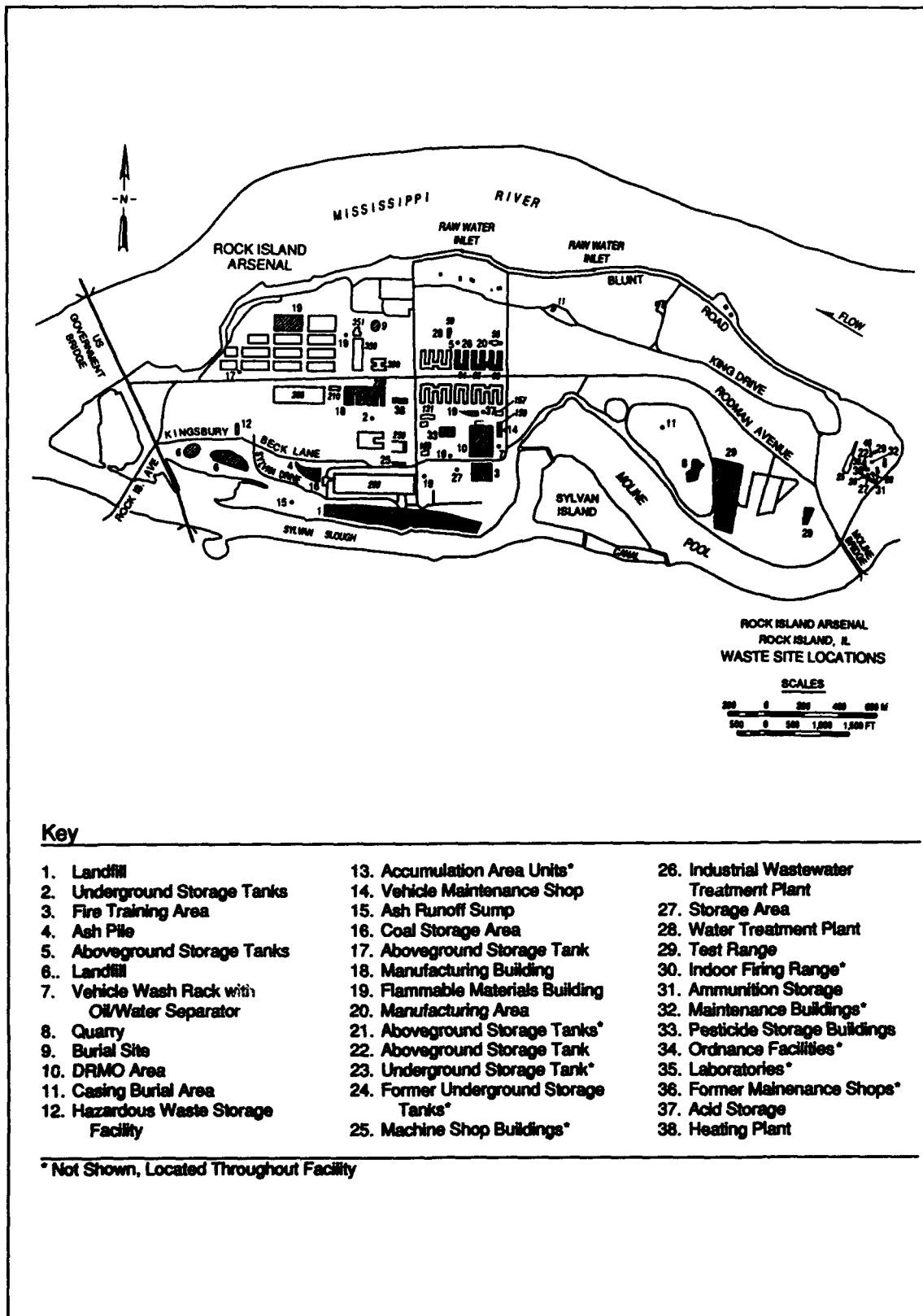


Figure 1. Rock Island Arsenal waste site locations

Table 9
Heavy Metals in Soil at Rock Island Arsenal—Buildings 64 and 66

Metals	Pile	West 66	NW 64	NE Corner 64	SE Entrance
pH (10% solution)	7.7	7.6	7.1	7.4	7.1
Lead	380	3100	1000	420	270
Chromium	20	26	7600	44	430
Cadmium	43.7	2.5	6.4	28 ^a	5.5
Copper	340 ^b	270	680	—	100
Nickel	37	42	140	36	58
Cyanide	0.82	0.62	2.6	7.6	10

Note: All results are average values and reported in µg/g. Results are total metals and total cyanide. Iron in all samples: 5,000 µg/g. All of the samples contained various types of material. None were homogeneous. The fine, dirt-like particles were used for analysis.

^a Average result of duplicates. Duplicate values were 19 and 38 µg/g.

^b Average result of duplicates. Duplicate values were 72 and 610 µg/g. All other duplicates were within 20 percent of the average values.

Metal contamination has also resulted from an ash pile and the coal storage areas where high sulfur coal was stored. A serious acid problem has arisen from the oxidation of sulfide to sulfuric acid at this site. The acid tends to dissolve the metals contained in the coal and ash. Thus, metals problems not only result from the ash, which contains high concentrations of metals, but from the migration and redeposition of metals in the soils surrounding the site.

White Sands Missile Range, New Mexico

WES Environmental Laboratory personnel visited the White Sands Missile Range (WSMR) in September 1991. They discussed metals contamination with WSMR and Lockheed contractor personnel at the High Energy Laser Test System Facility (HELSTF). Several samples of a highly contaminated chromium soil were collected.

WSMR personnel indicated the two significant areas of soil contamination were observed at HELSTF. The first was an area about 15 by 15 ft¹ contaminated with ENTEX-300, a water-conditioning agent with a high hexavalent chrome concentration. This area is located at the edge of the equipment "bone yard" (Cr Spill #143 Figure 2).

¹ A table of factors for converting non-SI units of measurement to SI units is presented on page viii.

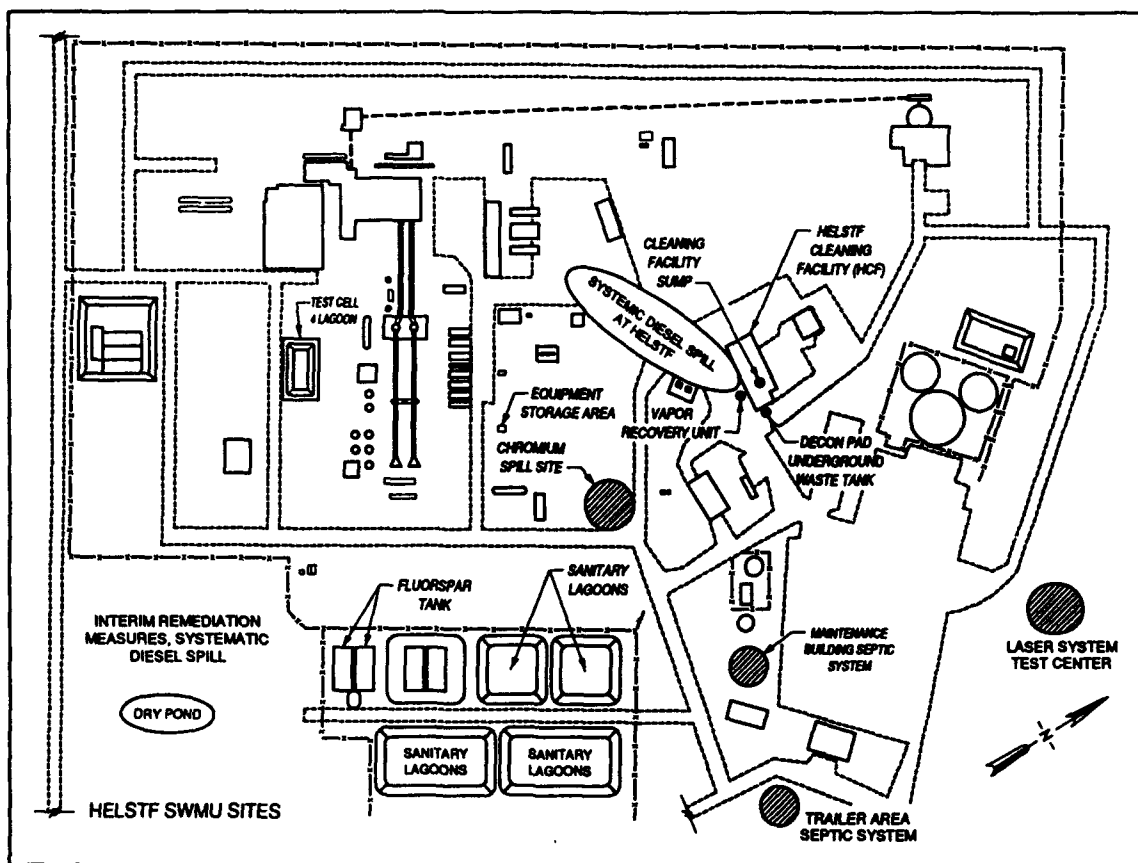


Figure 2. High Energy Laser Test Facility (HELSTF)—White Sands Missile Range

The second area is located beneath the foundation of a parts-cleaning facility. The soil under the facility is contaminated with cleaning solvents (e.g., trichloroethylene and freon) and metals. In addition to the contaminated soil at the site, WSMR personnel also indicated that metals had been detected in monitoring wells located near the HELSTF facility. The extent and spread of the contamination from these two sites is unknown, but WSMR personnel indicated there was a good possibility that widespread chrome contamination existed at the site.

Fort Ord, California

WES Environmental Laboratory personnel visited Fort Ord in September 1991 and met with personnel of the Directorate of Engineering and Housing. Discussions of the metals contamination at the facility focused on the rifle ranges. Fort Ord is scheduled to be closed, and the disposition of contaminated soil is a concern. There are a series of firing ranges that received heavy use during WWII and the Vietnam conflict eras. The whole series of ranges cover about 4.5 miles along the Pacific in an area of dunes forming a bluff overlooking the ocean. The dunes range from 25 to 30 ft in height, and the

front of the dunes sit about 0.5 miles from the ocean. The older ranges (numbered 12-17) have not been heavily used for several years. The active ranges are numbered 5, 6, and 7. Much of the expended small arms ordnance on the range complex is steel and copper-jacketed rifle bullets, but several of the pistol ranges contain nonjacketed lead slugs.

Soil samples were taken at Rifle Range 16 on the "North End" near the marina. Figures 3 and 4 show the overall layout of the range and sampling locations. Figures 5 and 6 show the significant lead particulate contamination as lead bullet slugs and fragments on and below the surface at the sampling area. Observation of WES personnel at the site indicates that the ranges contain heavy lead contamination. Lead fragments were found to be scattered over the entire surface of the dune. Lead fragments were also observed on the back side of the dune facing the ocean. Analysis of the soils indicated the TCLP leachate from the soils contain lead concentration in excess of 1,000 ppm and would be classified as hazardous.

Rocky Mountain Arsenal, Denver, Colorado

WES Environmental Laboratory personnel met with Rocky Mountain Arsenal (RMA) personnel including the Environmental Branch Chief. They toured the facility, obtained data on metals in soil, and made plans for RMA contract personnel to take samples and ship them to WES.

RMA personnel provided copies of site plans for the Basin A and M1 sites showing metals and organics concentrations. These plans show that the major metals contamination is attributed to arsenic, with soil concentrations reaching several thousand ppm. Other metals (mercury, chromium, lead, zinc, and copper) are also present in the soil at concentrations on the order of 10 to 100+ ppm.

While these contaminants were not migrating at a fast rate from the site of contamination, the USEPA is requiring RMA to take steps to ensure the contaminants will not have an environmental impact. Current treatability goals are to demonstrate a 90-percent reduction in the metals contained in TCLP leachate.

As a result of this visit, WES was tasked by the program manager at RMA to identify technologies that would be effective in treating the high levels of arsenic, mercury, and other metals. Subsequently, four soils samples contaminated with metals were shipped to WES. Because of the limited technologies available to address the treatment of metals, WES is currently conducting studies to evaluate the effectiveness of solidification/stabilization technologies for the remediation of this soil. In addition, WES recommended that studies be initiated to investigate the possibility of utilizing physical separation techniques for soil.

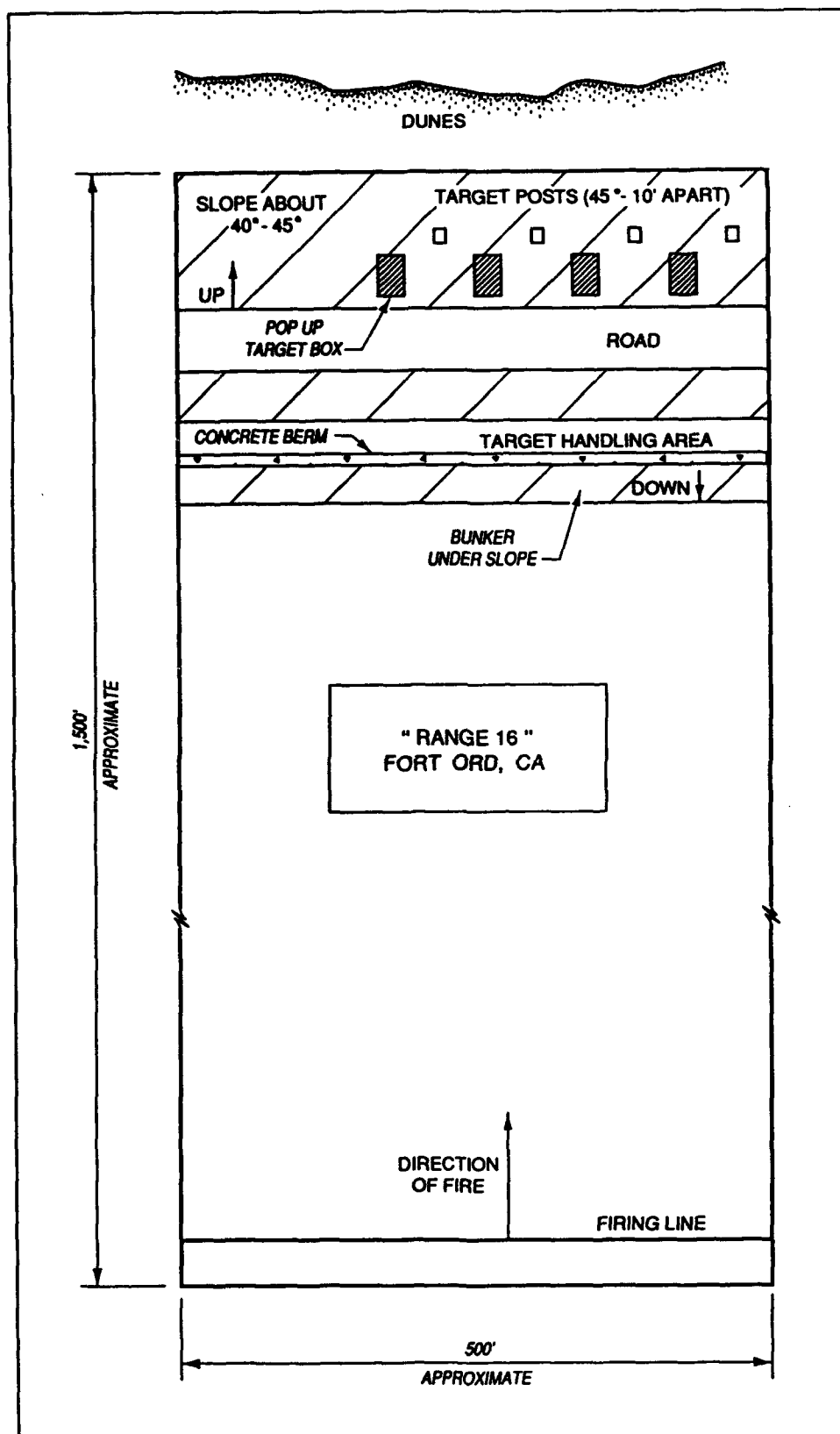


Figure 3. Firing Range 16, Fort Ord, CA

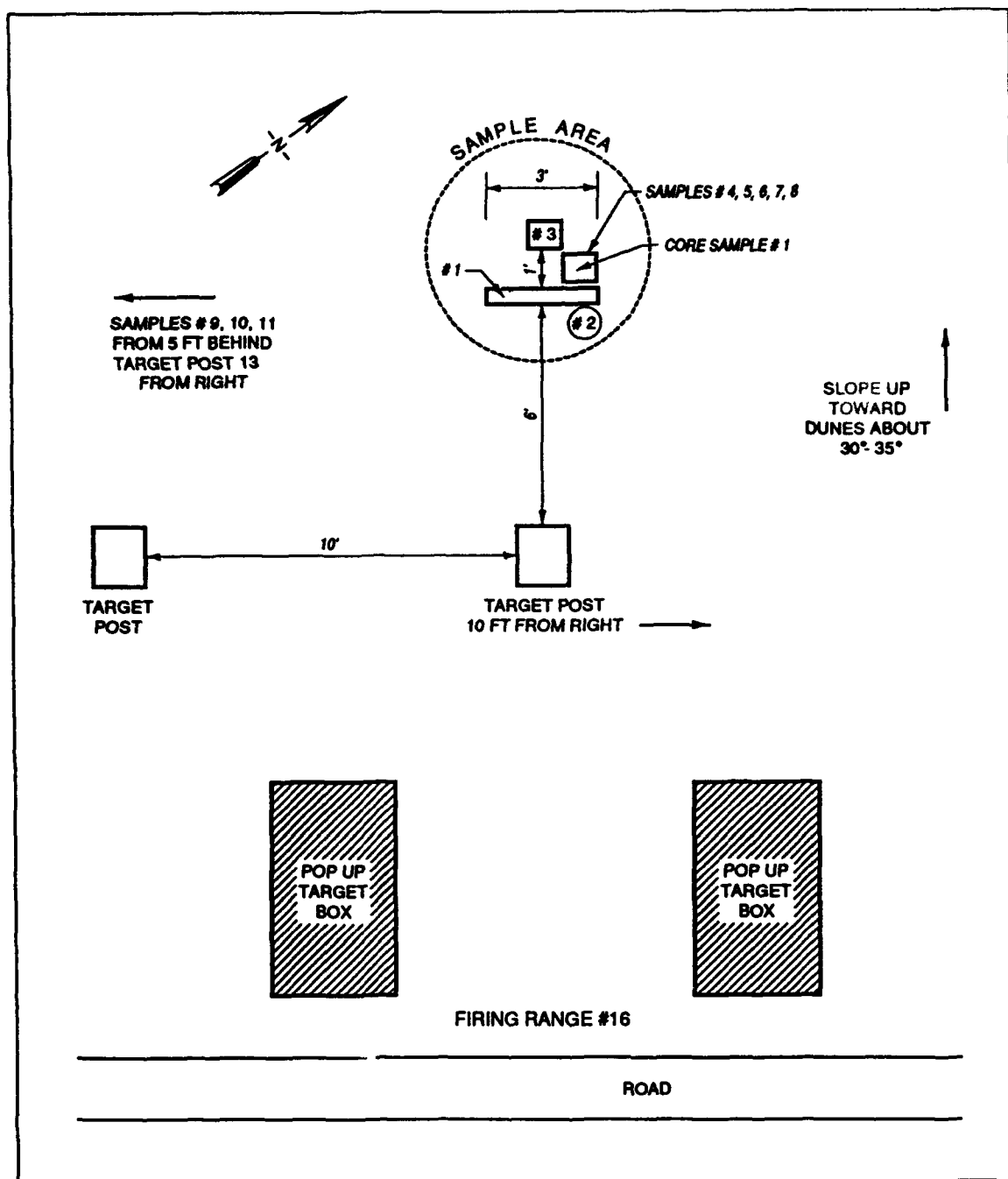


Figure 4. Sampling locations—Firing Range 16, Fort Ord, CA



Figure 5. Sampling in impact area, Rifle Range 16, Fort Ord, CA



Figure 6. Sample hole, Rifle Range 16, Fort Ord, CA

Umatilla Army Depot, Umatilla, Oregon

WES Environmental Laboratory personnel met with Umatilla Army personnel from the Environmental Branch. Discussions were conducted regarding metal contamination at the Depot. One source of metal contamination at this site was an Ammunition Peculiar Equipment (APE) Deactivation Furnace used to destroy small arms ammunition (generally referred to as a "popping furnace"). As a result of the ammunition demilitarization, various operations associated with the furnace and furnace emissions have resulted in significantly elevated lead levels (200 to 25,000 ppm) in the soil in a 1- to 2-acre area around the facility. The soil is classified as a hazardous material because it exceeds 5 ppm of lead in the leachate from the TCLP test, and action is required.

As a result of the lead contamination, WES was tasked by the Seattle District Corps of Engineers to perform studies to identify technologies for the lead-contaminated soil remediation. WES has received samples and has initiated solidification/stabilization testing to determine its effectiveness. In addition, WES is evaluating the effectiveness of physical separation techniques for the treatment of this soil. WES, under direction of the Seattle District Corps of Engineers, also plans to initiate studies to evaluate the effectiveness of metal extraction techniques for this lead-containing soil.

Conclusions

The study conducted by Weston (1987), as well as the WES update of this study and the surveys completed by WES, lead to the following major conclusions:

- a.* Many installations have soil contamination problems.
- b.* Chromium, lead, and cadmium were the metal contaminants most frequently found at military installations and are attributed to contaminating the bulk of metal-contaminated soil. At many installations, mercury and arsenic also are found, but generally contaminate smaller areas.
- c.* Soil concentration of chromium, lead, and cadmium often exceeded 20 times the TCLP limits. When this concentration is present, there is a high potential that the soils will be classified as hazardous.
- d.* There is a wide disparity of the status of assessment and remediation among facilities.
- e.* Firing ranges have received little assessment and have historically been of little concern. With the current problems associated with lead, regulatory agencies are taking a closer look at the firing range issues. Base

closure also is accelerating the need to address lead contamination problems. Firing ranges pose a large, difficult-to-handle problem with few available technologies that can be used for remediation.

- f.* Limited data exist on mobility of metals in soils at these installations.
- g.* The significant difference between soil properties and sludge waste properties makes it likely that numerous technologies will be necessary to address the variety of contaminants and contamination scenarios.
- h.* Fifteen of the twenty-four facilities surveyed by WES have metal contamination problems that will prove costly, difficult, or beyond current technology to remediate.
- i.* Facilities do not have adequate technologies to address the cleanup of heavy metal problems at this time.

3 Metal Contamination of Soils

Introduction

This chapter briefly discusses the scientific background of heavy metals contamination in soils and the major classes of treatment methods used to remediate soils. Topics addressed are the sources and forms of heavy metal soil contamination; metal/soil interactions; the association of the heavy metals with soil components; metal mobility as related to ion exchange, pH, and oxidation of organic coatings; physical metal transport with clay particles; and the mode of action of the major classes of treatment considered.

Long-term military and industrial practices have lead to heavy metal contamination in the form of sludges, contaminated soils and debris, and polluted surface and groundwater. Typical activities such as sandblasting, the use of lead-based paints, and firing range operations have produced soils contaminated with discrete metal fragments or metallic smears on soil particles. Electroplating, metalworking and refinishing, disposal of wastes in burning pits, munitions production, and cooling tower discharges have produced ionic forms of metal that associate with soil particles at the molecular level or are found in soil interstitial water.

Heavy Metal Interactions with Soil Particles

The primary parameters affecting the association of a heavy metal with soil and sediment include grain size and surface area, the nature of the geochemical substrate, metal species, and affinity of the metal for the soil as listed in Table 10.

Physical factors subdivide sediments or soils according to their physical properties: grain-size distribution, surface area, surface charge, density, or specific gravity. Chemical phase groups describe the different geochemical substrates that form the basis of the soil, such as carbonates, clay minerals, organic matter, iron and manganese oxides and hydroxides, sulfides, or

Table 10 Examples of Types of Physical and Chemical Partitioning		
Physical Factors	Chemical Interactions	Chemical Phase Groups
Grain size	Adsorption	Interstitial water
Surface area	Precipitation or coprecipitation	Carbonates Clay minerals
Specific gravity	Organometallic bonding	Hydrous Fe and Mn oxides
Surface charge	Cation exchange	Sulfides
Water content	Incorporation in minerals lattices	Silicates

silicates. Chemical interactions characterize the different types of association between metals and the geochemical substrates. The most important interactions are adsorption, precipitation, organometallic bonding, and incorporation into crystal lattices (Horowitz 1991).

Physical factors

A very strong correlation exists between decreasing grain size and the amount of heavy metal held by the soil fraction. It is one of the most important factors to be considered for concentrating and retaining heavy metals (Goldberg 1954; Horowitz and Elrick 1987). Soils and sediment collect, concentrate, and retain heavy metals largely by surface reactions or effects (Horowitz 1991).

Figure 7 illustrates the relative proportions of small and large particles contained in equal volumes. The surface area of the smaller spheres is much larger than that of the larger spheres. Likewise, Table 11 (Jackson 1979) shows surface areas per soil mass calculated for spherical particles of effective diameter. Note that the surface area would be two orders of magnitude greater for clay than for fine sand/coarse silt (Horowitz 1991). Real soil components are not spherical, but irregular and porous, and have greater surface areas than that estimated for spheres as shown in Table 11 (Forstner and Wittman 1981).

As particle size decreases, surface area per mass increases. Particle volume decreases as the cube of the radius, while surface area decreases by the square. Therefore, the surface area increases indirectly with the decrease in particle diameter (assuming spherical particles). Surface area is the most important property in interpreting chemical data, because it "integrates" all the surface effects of geochemical substrates such as surface charge and cation exchange capacity (Horowitz 1991). The demarkation line between very fine sand and coarse silt is defined at 63 μm . Recent research supports a strong correlation between total metals content and the metals content of the <63- μm fraction

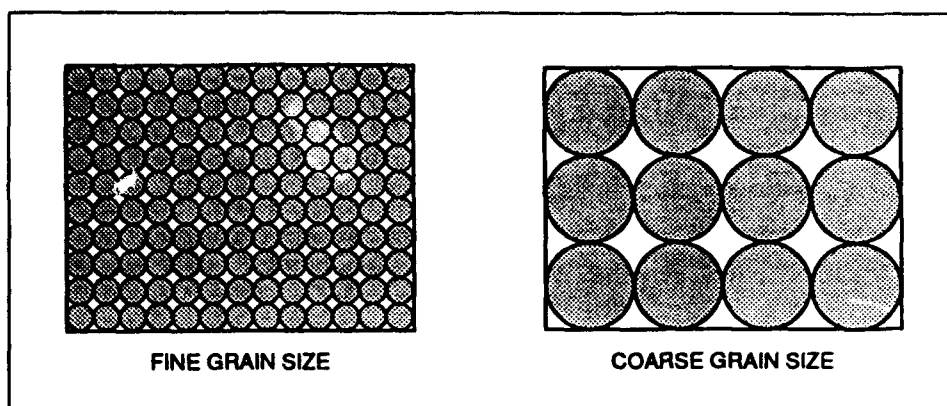


Figure 7. Increasing surface area with decreasing grain size

Table 11 Calculated Surface Areas for Soil Fractions, Assuming Spherical Shape				
Size Class	Diameter, μm	Volume, μm^3	Surface Area	
			m^2/g	cm^2/g
Very coarse sand	2,000	3.3×10^{10}	0.00113	11.3
Very fine sand/ coarse silt	62	1.0×10^6	0.036	360
Very fine silt/ coarse clay	4	263	0.57	5,700
Medium clay	2	33.5	1.13	11,300
Fine clay	0.5	0.52	4.52	45,280
Very fine clay	0.2	3.35×10^{-2}	11.3	113,000
Colloids	0.1	4.2×10^{-3}	22.6	226,400

(Horowitz 1991). Increased surface area per mass thus magnifies any tendency for geochemical substrates to collect metals.

Nonidealized clay particles are not spherical. They are typically thin platelets. Like the idealized (spherical) soils particles, as the particle size decreases, the surface area per mass of soil increases; but in clays, this phenomena is more pronounced. Typically, clay platelets increase a soils net surface area per unit mass by an order of magnitude over that which would be estimated using spherical particles occupying the same volume. Clay-sized sediments (<2 to 4 μm) have surface areas of tens of square meters per gram as illustrated in Table 12, while sand-sized particles have surface areas of tens of square centimeters per gram (Grim 1968; Jones and Bowser 1978).

Table 12
Measured Surface Areas of Selected Soil Components with
Diameters $<2\ \mu\text{m}$

Material	Surface Area, m^2/g
Calcite	12.5
Clay minerals	
Kaolinite	10 to 50
Illite	30 to 50
Montmorillonite	50 to 150
Iron hydroxide	300
Organic matter	1,900

As a practical example of the effect of increasing surface area for smaller particles, Table 13 (Horowitz 1991) shows how the concentration of copper in a marine sediment has been fractionated by particle size. The largest copper concentrations are measured in the smallest clay particles. As a result, copper retention on smaller particles contributes the majority of total metal retention. For example, clay makes up only 20 percent of the soil mass, but contributes 75 percent of the copper retention.

Data on the metal concentration distribution with particle size points out the importance of determining heavy metal concentrations for size fractions as well as for the bulk sample (Horowitz 1991). For example, two samples might have the same overall content of lead. The lead contained in a firing range soil would consist largely of lead particles, smears, and possibly metals exchanged or adsorbed to the soil's surface because of dissolution. A lead-contaminated sample from a battery reworking operation would have primarily adsorbed and ion-exchanged lead species held on the surface of the smaller particles. Such contamination partitioning will be dependant on how the soil was contaminated, the properties of the soil, and most likely would impact the choice of effective remediation treatment process.

Chemical factors

There are two major approaches used to characterize the association of heavy metals with soil and sediment (Horowitz 1991). The chemical interactions approach focuses on the different surface effects that absorb metals on soil particles. The five major mechanisms for the collection and retention of heavy metals in soil and sediment include the following: adsorption, precipitation and coprecipitation, organometallic bonding, and incorporation of the metals into crystalline minerals (substitution).

The phase approach identifies the type of geochemical substrates that interact with the heavy metals and characterizes the association of heavy metals in terms of the phase in which they are located. The most important phases are

Table 13
Distribution of Copper by Size Fraction in a Bottom Sediment Sample

Size Fraction, μm	Percent of Sample	Copper Concentration, mg/kg	Contribution to Sample, mg/kg
<2	20	750	150
2 to 6	15	60	9
6 to 10	18	110	19.8
10 to 20	30	60	18
20 to 32	10	25	2.5
32 to 64	7	20	1.4
Total	100		200.7

interstitial water, clay minerals, sulfides, carbonates, organic matter, hydrous iron and manganese oxides, and silicates.

According to Horowitz (1991), adsorption on the surface of the particle is the most important mechanism for the collection and retention of heavy metals. Adsorption can take place by physical adsorption, chemical adsorption, and ion exchange (Lieser 1975). Physical adsorption on a particle surface results from van der Waals forces or relatively weak ion-dipole or dipole-dipole interactions. Such reactions occur with iron oxides, aluminum oxides, clay minerals, and molecular sieves such as zeolites (Calmano and Forstner 1983).

Chemical adsorption involves formation of chemical bonds between ions or molecules in solution and the particle surface. An example is hydrolytic adsorption of ions from solution involved with a condensation reaction with OH^- groups on the surface of (silicon, iron, manganese, and aluminum) compounds (Calmano and Forstner 1983). Sorption-based ion exchange occurs when the soil/sediment adsorbs positively charged cations from solution, releasing equivalent amounts of lower affinity positive ions into the solution. Many heavy metals exist in solution as positive cations (except hexavalent chromium), while most soil/sediment materials have a negatively charged surface. The solid phase thus has a capacity for holding and exchanging cations, the "cation exchange capacity" (CEC) of the soil. In soil components, this effect is primarily due to the adsorptive properties of negatively charged anionic sites such as $\text{Si}(\text{OH})_2$, $\text{Al}(\text{OH})$ (clay minerals), FeOH (iron hydroxides), and COOH and OH (organic matter) (Forstner and Wittmann 1981; Horowitz 1991). The type of adsorption is affected by the composition of the geochemical substrate.

The geochemical substrates that are most important in collecting and retaining heavy metals are those that occur in abundance and that have large surface areas and high ion exchange capacities. In sediments, these active substrates

are usually thermodynamically unstable, and are amorphous or cryptocrystalline (Jones and Bowser 1978). The most common substrates in freshwater sediments are hydrous iron and manganese oxides, organic matter, and clay minerals (Horowitz 1991). Similar substrates are found in soils. Horowitz and Elrick (1987) have listed various substrates in descending order for their capacity to collect and concentrate heavy metals:

Amorphous Iron Oxides
Total Extractable Iron
Total Organic Carbon
Reactive Iron
Clay Minerals
Total Extractable Manganese
Manganese Oxides

Iron and manganese oxide. Iron and manganese oxides are well-known scavengers of heavy metals (Goldberg 1954; Krauskopf 1956). These phases are thermodynamically metastable and exhibit extensive isomorphic substitution (Jones and Bowser 1978); they are typically fine grained, amorphous or poorly crystallized and have a large surface area, high cation exchange capacity, and a high negative surface charge. In soils and sediments, the iron and manganese oxides also commonly occur as coatings on minerals and finely dispersed particles (Forstner and Wittmann 1981; Calmano and Forstner (1983)). Surface areas are on the order of 200 to 300 m²/g (Fripiat and Gastuche 1952; Buser and Graf 1955).

Organic matter. Organic matter in soils and suspended and bottom sediments have a large capacity to concentrate heavy metals (Goldberg 1954; Krauskopf 1956; Horowitz and Elrick 1987; and Hirner, Kritsotakis, and Tobschall 1990), concentrating metals such as cobalt, copper, iron, lead, manganese, molybdenum, nickel, silver, vanadium, and zinc to between 1 and 10 percent of dry weight (Swanson et al. 1966; Hirner, Kritsotakis, and Tobschall 1990). Aquatic and soil organic matter usually exhibits a large surface area, high cation exchange capacity, and a high negative surface charge. It is also capable of physically trapping the metals. The simple correlation of organic matter with decreasing particle size and increasing surface area is complicated, since organic surface coatings tend to concentrate in the smaller size fractions and discrete particles in the coarse size fraction (Horowitz and Elrick 1987).

Sorption of metals onto organic substrates occurs in one of three ways (Hart 1981): (a) from the action of organisms such as bacteria and algae; (b) from decomposition of plant and animal matter and the condensation of lower molecular weight organics; and (c) from sorption of lower molecular weight organic matter onto clay or metal oxide substrates (Davis 1980; Tipping 1981). Metal species may be adsorbed directly, or react with the organic materials to form organometallic species that are adsorbed. Major organic molecules that are active appear to involve salicylic entities and peptides (Lieser 1975) and carboxylic and phenolic groups (Tipping 1981). The

capacity of the soil to concentrate heavy metals is related to these characteristics as well as to the stability of the organometallic complexes (Horowitz 1991). The Irving-Williams (Irving and Williams 1948) series for soils gives the relative stability of organometallic species in descending order of the metal involved:

Lead
Copper
Nickel
Cobalt
Zinc
Cadmium
Iron
Manganese
Magnesium

Clay minerals. Clays act as important collectors and concentrators of heavy metals (Goldberg 1954; Krauskopf 1956; Forstner and Wittman 1981; and Horowitz and Elrick 1987). Clays are typically fine grained with large surface areas and a moderate to high CEC because of their large negative surface charge. The high CEC and surface charge result from broken bonds on mineral edges and substitution of Al^{+3} for Si^{+4} . This substitution causes a net negative charge in the clay lattice that is compensated by a positive (and typically exchangeable) cation. The capacity for heavy metals adsorption varies with clay type. Examples in order of decreasing CEC are as follows (Hirst 1962):

Montmorillonite > Vermiculite > Illite = Chlorite > Kaolinite

Likewise, the affinity of heavy metals for clay surfaces varies with metal type and are listed below in descending order (Horowitz and Elrick 1987).

Lead > Nickel > Copper > Zinc

However, the main role of clays in metals adsorption stems from their large surface area, which supports thin coatings of other substrates. Organics and hydrous iron and manganese oxides will flocculate and precipitate upon the clay surface so that the clay acts primarily as a mechanical support. The substrates coated onto the clay surface then are responsible for the adsorption of the heavy metals (Jenne 1976; Forstner and Wittman 1981; Horowitz and Elrick 1987).

Implications for Bioavailability, Stability, and Mobility

Bioavailability

Calmano and Forstner's (1983) study on sequential extraction of heavy metals from sediments suggests that the metal contaminants introduced into the aquatic system from anthropogenic (human) activities usually exist in relatively unstable chemical forms. Therefore, they should be more accessible for short-term and middle-term geochemical processes such as biological uptake than the more stable detrital and/or naturally occurring metal compounds. The estimation of bioavailability requires a combination of chemical extraction and biological experiments (Calmano and Forstner 1983). Studies by Jenne and Luoma (1977) and Luoma and Bryan (1978, 1979, and 1981) show that the bioavailability of heavy metals is inversely related to the strength of metal-particle binding in the sediments.

Plant roots extract nutrients from soil by redox reactions (Chaney, Brown, and Tiffin 1972), pH alteration (Moore 1974), and organic complexing processes (Calmano and Forstner 1983). The simulation of these mechanisms by sequential extraction experiments may provide information on bioavailability for soils and metals of interest.

The amount of exchangeable heavy metals is typically very low (Calmano and Forstner 1983). The most important enrichment phases (in sediments) are the easily and moderately reducible components, e.g., iron/manganese oxyhydroxides. Carbonate phases may also accumulate multivalent metal ions (Forstner and Patchineelam 1980).

Stability

As discussed above, the bioavailability of soil-sorbed metals depends on the properties of the particle's surface, the type of bond, and external conditions including pH, Eh (the redox potential), salinity, and the concentration of organic and inorganic complexing agents (Calmano and Forstner 1983). External conditions also affect the stability of minerals and the solubility of solution species. In a theoretical case study for arsenic minerals, Sadiq, Zaidi, and Mian (1983) estimated the proportions of arsenic species as affected by pH and redox state. Table 14 shows the predominant arsenic species as a function of pH and redox state.

Mobility

Heavy metals can be mobilized in one of two basic ways. First, the soil particles with adsorbed metals can be mechanically carried by water, air, or human or animal activities. Second, changes in redox state, pH, or organic

Table 14
Arsenic Species as a Function of pH and Redox State

System Condition	Most Stable/Predominant Species
Oxygenated and alkaline	$\text{Ca}_3(\text{AsO}_4)_2$ and $\text{Mn}_3(\text{AsO}_4)_2$ (Probably as precipitates)
Reduced and acidic	As (III) oxides and sulfides (Unstable above $\text{pe} + \text{ph}$ of 8) ¹
Oxidized solutions ($\text{pe} + \text{pH} > 8$)	Arsenate species
Reduced solutions ($\text{pe} + \text{pH} < 8$)	As (III) in abundance
$\text{pH} < 2.2$	H_3AsO_4^0 in abundance
Increasing above pH 2.2	H_2AsO_4^- important
$\text{pH} > 12$	AsO_4^{3-} important

¹ pe and pH are the negative logarithms of redox potential and H^+ molarity.

Table 15
Percentages of Elements Transported in the Dissolved Phase During River Transport

99%	99%							50%									10%	5%							
Cr	Br	S	Na	Sr	C	Ca	Li	Sb	Mg	N	B	Mo	As	F	Ba	K	Cu	P	Ni	Si	Rb	U	Co	Cd	
Mn	Th	V	Cs	Ga	Pb	Lu	Ti	Gd	La	Ho	Yb	Er	Sm	Cr	Fe	Eu	Ce	Zn	Al	Sc	Hg				
				1%				0.5%														0.1%	0.5%		

composition of the interstitial solution can convert species to a more soluble form or can cause adsorbing phases to release the metals to solution and subsequent transport by ground or surface water. Transport by water has been widely studied in the polluted sediment transport area. In rivers, heavy metals transport in the dissolved phase is a predominant transport mechanism as shown by the data of Meybeck and Helmer (1989) in Table 15.

The affinity of metal ions for the soil particle surface plays an important role in the chemical "remobilization" of metals from soil particles. Calmano and Forstner (1983), who studied mobilization of heavy metals by a five-stage sequential extraction, found that a much greater proportion of zinc and cadmium were extracted than were lead and copper, which have higher affinities. This also agrees with extraction results using sludge amended soils (Cottenie and Kiekens 1981). Likewise, in extraction experiments using weak extraction agents such as ammonium acetate and ammonium nitrate, a better correlation is found between plant uptake and extractability for cadmium and zinc than for lead with its higher affinity (Calmano and Forstner 1983; Leeper 1978; and Sterritt and Lester 1980).

Mode of Action of Soil Treatment Technologies

As previously described, heavy metals are predominantly associated with smaller, higher surface-area particles. They preferentially adsorb (or coprecipitate) with hydrous manganese and iron oxides, organics, and clay minerals. The tendency of metal ions to associate with distinct soil/sediment fractions offers opportunities to selectively effect physical separation to treat soil contaminated by heavy metals. Additional chemical, physical, or biological methods can then immobilize the metals or separate them from the particles. The following sections briefly describe the mode of action for a few of these approaches.

Physical/chemical processes

Physical/chemical processes include those that remove or immobilize metals in soil by application of chemical or physical (mechanical) action or electrical potentials. Heavy metals can be immobilized in the soil by chemical precipitation. Likewise, chelating agents and acids can remove metals by displacing (or ion exchanging) them from the soil into a liquid phase. Recent research has exploited the distribution of metals in soil/sediment by physically removing or screening out smaller contaminant-rich particles. Ideally, the "cleaned" fraction will require no further treatment, and the "concentrated" fraction can be more economically processed.

Thermal processes

Thermal processes include those in which the soil is heated to drive off or immobilize the metals in the soil. Thermal extraction may involve chemical conversion of metals to their more volatile chloride forms, followed by heating at a high temperature to remove the metals through vaporization. Other thermal techniques involve heating the soil so that fusible soil components soften and melt to coat and bind together metal-contaminated particles in a glass-like mass that is more resistant to leaching.

Immobilization/stabilization/disposal processes

Immobilization, stabilization, disposal processes include those that immobilize the metals in the soil with cement-like (Portland or pozzolanic) or polymeric compounds that bind the metal contaminants into the soil, decreasing the tendency to leach. Also included in this category are technologies such as geological isolation and deep well injection. These processes represent engineered scenarios that minimize contaminant migration through isolation. Generally, isolation treatment methods are only recommended when alternative methods are not available.

Vegetative uptake

Vegetative uptake methods include processes that remove metals from soil through plant root systems and concentrate the metals in the plant tissue. In the case of metals, the vegetation would require removal and further treatment, perhaps digestion or incineration to further concentrate metal contaminants.

4 Review and Assessment of Soil Cleanup Technologies

The first three chapters of this report review the origin, severity, and nature of soil contamination by heavy metals at military installations. This chapter briefly discusses the background activities leading to the development of the research strategy discussed in Chapter 5 of this report.

Review of Potential Soil Treatment Technologies

The WES review of soil treatment technologies was based upon an earlier study by Weston, Inc., which was completed in 1987 for USAEC. WES personnel updated and further evaluated the Weston review focusing upon the soil treatment technologies that were seen as the best candidates for research and development. The product of this investigation is the updated review that has been published as a companion report entitled "Technology Assessment of Currently Available and Developmental Techniques for Heavy Metals-Contaminated Soil Treatment" (Bricka, Williford, and Jones 1993). A list of the technologies covered in this report is presented in Table 16.

The report subdivided soil treatment technologies into various categories that can be grouped into three basic classes: (a) physical and chemical, (b) thermal, and (c) immobilization, stabilization, disposal processes. Each of the technologies was reviewed using a consistent format summarized below:

- a.* Description of the process including background theory, the current state of development, a compilation of available performance data, and a conceptual design schematic.
- b.* Treatment effectiveness assessing the actual or predicted performance based on results available in the literature and/or best engineering judgement. The treatment goal is to render the soils capable of passing the USEPA TCLP test for disposal as nonhazardous materials.

Table 16
Technologies Reviewed and Assessed

Physical/Chemical Processes Precipitation Extraction Adsorption Ion exchange processes High gradient magnetic separation Electrochemical separation Physical separation
Thermal High temperature fluid wall Roasting Thermal extraction Onsite plasma arc Vitrification
Immobilization/Stabilization/Disposal Solidification/stabilization Microencapsulation Macroencapsulation Secure landfill Geologic isolation Injection wells
Vegetative Uptake

- c. Long-term stability and performance, a determination of whether treatment performance is likely to have permanent, long-term effectiveness in rendering the soil nonhazardous based upon literature and/or engineering judgement.
- d. Residuals treatment/disposal requirements, identification of potential residual waste side streams (i.e., extract solutions) that will require further treatment and/or disposal because of expected hazardous properties.
- e. Adaptability. Assessment of the ability of the process to treat various soil/site types or other waste streams (i.e., sludges); to treat for organic compounds concurrently with metals; or to be readily linked to other processes for organic or explosive compound treatment.
- f. Scale up potential. An estimate of actual throughput rates and/or the anticipated ability to scale up the process.
- g. Potential disqualifiers. Identification of known or potential "fatal flaws" that could hinder development and implementation of the process, including the following:
 - (1) Inherently unsafe.

- (2) Uncontrollable environmental risk of mobilization.
- (3) Uncontrollable air emissions.
- (4) Prohibitively expensive.
- (5) Exceedingly complex materials handling, operation, or maintenance required.

In the original Weston study, a team of six knowledgeable reviewers were charged to assign numerical values to each of the screening criteria (except potential disqualifiers). In addition, weighting factors were applied to each of the selection criteria to represent their relative importance. Summing these products and averaging for the six reviewers resulted in a "consensus score" rating the relative potential of each technology to be successfully employed in soil cleanup. The reviewers rank of the technologies is shown in Table 17. Further assessment based on the potential disqualifiers and USAEC objectives at the time narrowed the field to three technologies felt to have the highest potential for development: microencapsulation, roasting, and onsite extraction.

Table 17 Technology Rankings by Weston Reviewers		
Rank	Technology	Score
1	Onsite vitrification	57.5
2	Microencapsulation	55
3	Roasting	54.5
4	Stabilization (admixing)	54
5	In situ vetrification	51
6	Geologic isolation	49
7	Secure landfill	48
8	In situ microencapsulation	46
9	Chloride volatilization	44.5
10	Macroencapsulation	41
11	Onsite extraction	40

WES Advisory Panel Review

Continuing the evaluation process, WES assembled a panel of 15 experts to discuss the applicability of a variety of technologies for the remediation of heavy metal-contaminated soils. They met in October 1990 at WES and were charged to (a) identify promising technologies for the treatment of heavy

metal-contaminated soils and (b) identify research needs necessary to field one or more of the promising technologies within 5 years. A list of participants is given in Appendix A.

Lengthy discussion addressed the difficulty of evaluating the technologies for general, undefined problems. For example, the cleanup of soil from a military firing range would differ from the cleanup of soil contaminated with electroplating sludge. This discussion led to the consensus that such issues were "site specific" but that the technologies could be discussed in relative terms by comparing their feasibility based on the panel's experience and expertise.

Another issue discussed was the desired cleanup levels of the technologies. The conclusion reached by the advisory panel was that each state or USEPA region might set different cleanup levels that would be site specific. The panel decided to focus on the applicability of the technologies without defining the cleanup levels or site specific considerations.

The meeting then proceeded with a detailed discussion of the technologies listed in the WES companion report (Bricka, Williford, and Jones 1993). A draft of this report was distributed to the workshop participants. Each treatment process was discussed individually and at length. A summary of the panel's deliberations about the treatment technologies is presented below.

Physical/chemical processes

Precipitation, extraction, adsorption, ion exchange, magnetic separation, and electrochemical separation processes were discussed at length. Both the above-ground (excavate and treat) and insitu treatment aspects of these technologies were discussed.

The panel felt that in situ precipitation is a technology that is not field implementable in 2 to 4 years, although phosphate precipitation may offer some unique possibilities in this area. The panel also concluded that precipitation technologies must be used in conjunction with other technologies (e.g., extraction) to be applicable for soils cleanup. Further investigation of precipitation technologies may be necessary as part of the investigation of other technologies. Of the precipitation technologies, sulfide and sodium borohydride treatment techniques either produce a hazardous sludge or may cause difficult-to-control side reactions that disqualify these processes from further consideration. Hydroxide precipitation on the other hand has been studied extensively, but it was felt that additional limited research may be warranted. Vapor phase precipitation with SO_2 was attractive for in situ evaluation but was limited to chromium reduction. Little work has been done with xanthate precipitation and further research appears warranted.

Of the technologies discussed under this major topic area, electrochemical separation and extraction technologies were the technologies considered most feasible for additional research.

Extraction technologies for the removal of metals from soils were rated as the physical/chemical process with the highest potential for success, with field implementation of the technologies in the near future highly feasible. It was pointed out that many mining techniques for the separation of soils were available and merited consideration. The group agreed that if the metals-contaminated soils were associated with a particular fraction (i.e., clays or fines), this technology could be very helpful in reducing treatment costs. Therefore, in addition to extraction technologies, separation technologies were also recommended for additional evaluation.

Thermal processes

High temperature fluid wall reactors, roasting, chloride volatilization, onsite plasma arc, and in situ and onsite vitrification technologies were discussed. It was determined that thermal technologies cannot be compared with non-thermal technologies without looking at all side streams of the thermal processes. Heavy metal and volatile emissions, as well as potentially hazardous ash, require additional handling that may increase long-term liability and increase disposal costs.

The consensus of the panel was that R&D of high temperature fluid wall reactors, onsite plasma arc, and onsite vitrification technologies were not applicable for consideration under this program because of technical or economic considerations. In situ vitrification was also not considered appropriate for consideration under this program because of the fact that USAEC considered this technology to be "fully developed." In summary, emphasis was placed on roasting (or slagging) technology for metals containment, and chloride (or enhanced) volatilization should be considered appropriate under this program.

Immobilization/stabilization processes

Stabilization, microencapsulation, macroencapsulation, RCRA landfilling, and geologic and engineered structures (entombment) were discussed. Macroencapsulation and geologic isolation were eliminated from further consideration because of the fact that they were not truly metal treatment technologies but simply containment technologies. After a lengthy discussion, stabilization and microencapsulation were (for the purposes of discussion) considered by the advisory panel participants to be the same technology.

The workshop participants felt that stabilization/microencapsulation technology was already in widespread use. Although it is currently being used to clean up metal-contaminated soil, the committee discussed many areas where further research was needed, including the development of better procedures

for predicting performance, such as leaching and physical tests; investigation into the fundamental mechanisms of the process; and long-term testing and evaluation procedures. Because of the shortcomings, it was the consensus of the committee that physical, chemical, and thermal immobilization processes should be considered a high priority and R&D be initiated in this area.

Another technology grouped and discussed under this category was geologic disposal including RCRA landfills and engineered containment structures. As with the solidification/microencapsulation technologies, the consensus of the workshop participants was that there were many research needs associated with RCRA landfills. However, it was felt that R&D directed towards geologic isolation areas did not fall within the scope of this program.

Other technologies

Two major technologies were discussed under this major heading: vegetative uptake and biometals uptake. Both technologies were discussed at length. As a final result, the workshop participants agreed that both technologies would have limited application for the cleanup of heavy metal-contaminated soils. Vegetative uptake would be limited to the root zones of the plants, and biometals uptake would take a very long time for treatment to be effective. In addition, a removal mechanism for the organisms needs to be developed.

Summary

The advisory panel participants felt that the companion report (Bricka, Williford, and Jones 1993) covered most of the technologies worthy of discussion. After thorough discussion of each technology, the advisory panel concluded that the physical/chemical/processes (extraction in conjunction with separation technologies) and the thermal processes (roasting and enhanced volatilization) warranted further research under this program. These panel recommendations in conjunction with the Weston evaluation form the basis of the research strategy for metal-contaminated soils presented in the next chapter of this report.

5 Research Strategy for Metal-Contaminated Soils

Research Needs for Remediation of Metal-Contaminated Media

Serious contamination of various media (soils, sediments, and structures) by heavy metals has been found to occur at a majority of Army installations. Metals such as chromium, cadmium, lead, zinc, mercury, and arsenic are found to contaminate structures, groundwater, and soils and emanate in leachate from accidental spills, open and closed landfills, and other disposal operations. Efficient and cost-effective technologies are needed for detoxifying, immobilizing, and/or removing metals and providing permanent remediation solutions.

This study has identified three major research areas that address the significant needs of a typical Army installation. The research areas were selected after an extensive literature review, surveys of appropriate personnel, site visits to selected military installations, and the consideration of recommendations of the WES and Weston Advisory Panels on metal-contaminated soils.

Nine specific work units were developed as a result of this effort. These work units were developed to directly support the difficulties of the three major research areas. The major research areas and each work unit are presented below.

Research Area 1. Determination of Metals Partitioning, Speciation, Mobility, and Mass Transport Relationships and Mechanisms

Work Unit Methodology for Characterizing Metal-Contaminated Soils, Liquids, and Structures.

Work Unit Evaluation of Strategies for Minimizing Mass Transport Limitations to Heavy Metals Recovery and Treatment.

Research Area 2. Development and Enhancement of Metal-Recovery Technologies

Work Unit Physical Separation Techniques for Bulk Soils and Structures.

Work Unit Treatment of Metal-Contaminated Groundwaters, Liquids, and Extracts.

Work Unit Treatment Methods for Removing Metals from Contaminated Soils and Structures.

Work Unit In Situ Extraction and Fluid Delivery Techniques.

Work Unit Heavy Metal Decontamination of Soil Using Electrochemical Transport Processes.

Research Area 3. Development and Enhancement of Metal Immobilization Technologies

Work Unit Chemical and Thermal Immobilization techniques for Metal-Contaminated Media.

Work Unit Biological Stabilization of Heavy Metal-Contaminated Soils.

Detailed Research Work Unit Descriptions

The research work units are listed below in order of priority. The priority is based upon the importance of the topic to the authors' understanding and the development of metal treatment technologies. For each proposed work unit, the title, objective, and technical approach are briefly noted.

Work Unit 1. Methodology for Characterizing Metal-Contaminated Soils, Liquids, and Structures

OBJECTIVE: Development and/or refinement of existing methods for modeling and characterizing the distribution and speciation of metals in soils and other solid and liquid media to support development of improved treatment techniques and evaluation of their effectiveness.

APPROACH: Identification of the various chemical and physical forms, distribution, and speciation of heavy metals in metal-contaminated soil and liquid is necessary for the development of successful treatment technologies. Such work is needed to support development of improved treatment techniques such as metals extraction, thermal treatment, electrochemical treatment, and

solidification/stabilization. At present, the ability to develop and implement such treatment technologies is limited by a lack of understanding of the basic processes governing the distribution of metals in soils, solids, and liquids. For example, metal speciation as well as soil/metal interaction must be known before the solids can be treated effectively. An increased understanding of metals distribution, form, and speciation in soils and solids will provide needed information to aid in the development of effective treatment technologies. The ultimate goal of this work unit is to provide tools that can be used to predict the performance of a treatment technology beyond the currently used and limited treatability study approach.

This research effort will evaluate techniques for determining metal distribution, form, and speciation in a wide variety of media and focus on their applicability to metal treatment technology development and performance. Techniques for tracking metal mobility such as radiotracer techniques, sequential batch extractions, column leaching, and advanced analytical chemical techniques and instrumentation will be investigated.

Work Unit 2. Evaluation of Strategies for Minimization of Mass Transport Limitations to Heavy-Metals Recovery and Treatment

OBJECTIVE: Development of operational strategies for minimizing mass-transfer limitations to heavy metal recovery technologies for subsurface remediation.

APPROACH: Recovery of heavy metals from subsurface environments by pump/extraction technologies is limited by preferential flow of water at macroscopic and microscopic scales. At the macroscopic scale, preferential flow of water because of soil fabric limits access of extraction fluids to contaminated zones in the soil profile. At the microscopic scale, immobile water films on individual soil particles, immobile water in soil aggregates, and immobile water in intraparticle pores provide diffusive mass-transfer resistances to the transfer of heavy metals from contaminated soil surfaces to extraction fluids. To overcome these limitations, a basic understanding of the relative significance of each type of limitation is needed. Determination of the extraction rate limiting resistance will provide the basis for development of operational strategies for minimizing mass-transfer limitations.

This investigation strategy will involve batch testing to investigate intraparticle and film resistances and column testing with undisturbed and packed columns to investigate soil aggregate and fabric resistances to heavy metal recovery. Both batch and column studies will use anthropogenically (by human activities) contaminated soils from field sites. Batch studies will use various shaking regimes from mild to very vigorous agitation and chemical reaction engineering models to evaluate film and intraparticle resistances to mass transfer. Undisturbed and packed column studies are needed to separately evaluate soil aggregate and fabric resistances. Soil aggregate and fabric resistances will be investigated at various pore water velocities to provide

information on reaction kinetics for heavy metal extraction. Operational strategies such as pulsed pumping will be investigated in the column tests. In addition, facilitated extraction using naturally occurring organic colloids will be investigated in batch and column studies. Data from batch and column studies will be integrated to provide fundamental insight into hydrochemical factors affecting heavy metals recovery from contaminated soils.

Work Unit 3. Physical Separation Techniques for Bulk Soils and Structures

OBJECTIVE: Evaluation and refinement of existing physical separation techniques for use as pretreatment of excavated bulk soils and construction debris prior to secondary processing.

APPROACH: Metals generally associate in soils with the small-size fraction of particles, especially in soils with high clay and/or organic matter content. In addition, military firing ranges often possess soils contaminated with large lead projectiles. Physical separation technologies offer a cost-effective method for removing large fractions of total metal from soils and construction materials.

The potential of using existing separation techniques for the removal and segregation of the portion of soils contaminated with heavy metals will be investigated. Existing soil processing and separation equipment, such as spiral classifiers and hydrocyclones, will be evaluated. Metal-contaminated soil samples will be collected and a determination of the metals' distribution and mobility in the soil fractions will be made. Equipment will be purchased and tested in the laboratory to determine the feasibility of such separation technologies. Promising technologies will be evaluated in a field demonstration project.

Work Unit 4. Techniques for Treatment of Metal-Contaminated Groundwater, Liquids, and Extracts

OBJECTIVE: Development of cost-effective technologies and processes for the treatment of metal-contaminated liquids and extracts generated during the decontamination of metal-contaminated structures and soils.

APPROACH: Treatment technologies and processes, such as ion exchange, reverse osmosis, and precipitation techniques, currently exist for the treatment and purification of water and wastewaters. In many instances, strict water treatment standards have rendered or will render many treatment systems inappropriate for the treatment of liquids resulting from the extraction of soils contaminated with heavy metals. Treatment and reuse of extraction liquids generated during the remediation of metal-contaminated structures and soils also require special attention. In many cases, the wash water generated during metal extraction contains complexing agents (such as

ethylene-diamine-tetracetic acid (EDTA)), which will make the removal of metals from the wash water especially difficult. In addition to removing the metal from the extract, techniques must be developed to separate and recycle the extraction fluid to make the process cost effective. Groundwater treatment that is to be reinjected may also pose unique treatment problems.

This research effort will investigate the applicability of existing metal treatment processes for treatment of heavy metal-contaminated liquids and extraction fluids. If these methods prove to be ineffective, research to address shortcomings will be initiated. In addition, research to develop and refine new methods such as biological sorption, emulsion separation, and hollow fiber membrane techniques for treatment of heavy metal-contaminated metal extracts will be investigated. This effort will result in pilot-scale field evaluations of the most promising technologies.

Work Unit 5. Evaluate Treatment Methods for Removing Metals from Contaminated Soils and Structures

OBJECTIVE: Determination of procedures for the optimum removal of metals from soils and structures and the development of technologies to optimize metal removal.

APPROACH: This work unit will develop treatment technologies for removing metals from contaminated soils and structures so that the treated soil or material may be backfilled without additional special handling. At present, such techniques are undergoing emerging development and are useful only in limited cases. This investigation will approach the problem in a systematic manner, combining basic and applied research to develop and test the effectiveness of treatment technologies involving the removal of the metals from solid media. This work will result in cost-effective treatment technologies for solid media that will have nationwide applicability for metal contamination problems.

This research effort will focus on development of extraction technologies for solid media. Extractants will be identified and tested to determine their effectiveness. The effects of operating parameters such as length of extraction time, temperature, pH, and pressure on extraction effectiveness will be investigated. Addition of chemicals to the solid media prior to extraction to increase efficiency will be investigated, as will sequencing of extractants to assist in efficient metal removal. The most promising procedures and extractants identified as technically feasible at the bench level will be transitioned to the pilot level to evaluate their engineering feasibility and costs. Material handling and processing schemes for increasing the mobility of the metals will also be investigated. Successful treatment schemes will be field demonstrated.

Work Unit 6. In Situ Extraction and Fluid Delivery Techniques

OBJECTIVES: Evaluation and development of technologies for the injection and extraction of fluids required for implementation of in situ technologies.

APPROACH: Currently the ability of "pump and treat" systems is limited. Previous studies have uncovered a number of limitations with existing fluid removal systems. This investigation will focus on identifying the shortcomings of existing fluid removal systems and will develop techniques to overcome such problems. One concept will involve the use of the cone penetrometer as a rapid method to install injection and recovery well points. If existing equipment is deemed inefficient, then retrofitting the existing equipment will be investigated. The results of this effort will be applied in field demonstrable systems.

Work Unit 7. Chemical and Thermal Immobilization Techniques for the Treatment of Metal-Contaminated Media

OBJECTIVE: Development of improved technologies for the immobilization of metals in soils, structures, and groundwater media and a better understanding of the chemical, thermal, and solid media properties controlling the effectiveness of such procedures.

APPROACH: Chemical immobilization technologies such as solidification/stabilization (S/S) have been used on a wide scale for the remediation of heavy metal-contaminated materials. However, the factors governing the effectiveness of such procedures are not well understood. Furthermore, the long-term performance of these materials has not been effectively addressed. A better understanding of the mechanisms controlling S/S processes and improvement in treatment effectiveness is necessary if these techniques are to be of future usefulness.

In addition to chemical immobilization techniques, thermal immobilization technologies have a high potential for the treatment of metal-contaminated media. Unfortunately, thermal processes (such as vitrification) have only been demonstrated on a limited scale for hazardous waste or metal-contaminated soils. Research is needed to investigate the feasibility of both chemical and thermal immobilization techniques for the containment of heavy metals. Research will be conducted to gain a better understanding of the mechanisms responsible for the effectiveness of immobilization technologies. Various admixtures will be formulated, and the effects of these admixtures on the metal mobility of S/S soils will be evaluated. Pretreatment for immobilizing and/or changing metal speciation prior to chemical treatment will be evaluated. Long-term physical and chemical immobilization performance of immobilized materials will be evaluated in both the laboratory and the field. The potential of chemical precipitation curtains for containment of metals will be evaluated in a large-scale study. Using a hydraulic gradient, metal contaminants will be

transported to the curtain, and transport properties of the metals through the curtain will be developed.

Thermal immobilization technologies research will be conducted to determine the effects of physical parameters such as soil moisture, soil composition, and system-operating temperature on performance. Such information will enable optimal control of the thermal system to ensure efficient metal immobilization in the ash or slag that is produced. Detailed material and energy balances for the process will be conducted to determine if metals loss is occurring in stack gas and to calculate the economics of the treatment system. Because of the fact that metals in the stack gas emissions may pose an environmental risk (or possible removal route), research will be conducted that focuses on trapping of metals prior to their loss to the atmosphere. Existing procedures will be closely investigated and deficiencies will be documented. In addition, improved technologies will be developed to trap volatile metals.

Work Unit 8. Heavy Metal Decontamination of Soil Using Electrochemical Transport Processes

OBJECTIVE: Evaluation of the feasibility and effectiveness of electrochemical transport processes for treating metal contamination problems in soil environments.

APPROACH: Limited basic research has shown that electrochemical transport processes have the potential to extract heavy metals from contaminated soils. This technique is a promising method for the *in situ* removal of metals from contaminated soils, but additional research is required. Research is needed to determine the efficiency of the procedure for treating metals, overcoming operational problems, and demonstrating this technology in the field.

This research effort proposes to investigate the movement of water and metals in a variety of media through soils in the laboratory. The procedure will also be tested to determine if fluids that extract metals from solid media can be moved through soil by electrochemical processes. This research will enable the mass-transfer limitations of the systems to be determined and will provide information on system effectiveness and costs. In addition to investigation of the effects of the electrochemical potential on the removal of metals, a hydraulic gradient will be induced on the system to determine its effects. If the laboratory tests indicate a potential of field success, an "undisturbed" metal-contaminated soil sample will be collected, and testing will be initiated to determine the effectiveness of the system under simulated field conditions.

Work Unit 9. Biological Stabilization of Heavy Metal-Contaminated Soils

OBJECTIVE: Develop in situ biological stabilization and immobilization techniques for heavy metals.

APPROACH: Heavy metal contamination will be managed in situ using biological stabilization techniques. Management strategies that use soil amendments and plant species to vegetate and stabilize a contaminated site will be evaluated for preventing the migration of heavy metals in surface runoff, into groundwater, or into foodwebs associated with the site. Basic research in the form of laboratory/greenhouse experiments will (a) screen and determine the more effective soil amendments and plant species that prevent migration of heavy metals from a site and (b) quantify the maximum concentration of heavy metals that can be stabilized by biological methods. Soil amendments such as lime, fly ash, basic slag, manure, leaf litter, tree bark, and/or sewage sludge will be evaluated for potential use. Plant species that are tolerant to heavy metals, but are effective for soil erosion control, will be evaluated. Plants that transpire large amounts of moisture and tend to dry soils will be evaluated for reducing leachate to groundwater. Limited research along these lines has been conducted in the United Kingdom and appears to be effective for site conditions tested in the United Kingdom.

Developmental research will also be conducted in the form of larger scale experiments using simulated rainfall/soil bed lysimeter tests to confirm and quantify the migration of heavy metals from vegetated amended soil. Bioassays will be conducted on surface runoff water to evaluate the biological effects of runoff water. Plant and earthworm bioassays will be conducted on amended soil to evaluate migration of heavy metals into groundwater. Demonstrations of the most effective soil amendment(s) and plant species combinations will be conducted in the field at specific sites contaminated with heavy metals.

Summary

This research strategy with its attendant priorities embodies our best judgment of the most efficient path to a rapid understanding and development of new and innovative technologies for treating metal-contaminated soils as well as other media. It is based upon an analysis of the extent and severity of the Army's metal-contaminated media, the combined opinion of experts in the field, and WES's own field experience.

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Appendix B

WES Survey: Points of Contact and Installation Lists

Initial Installations List for WES Survey

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Source: Environmental Management-By-Objectives (MBO) Report RCS DD-M (SA)-1485.

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Fort Hood	Bill Bodkin	(817) 287-6499
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Lone Starr AAP	Art Fokakis	(903) 334-2161
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Rocky Mountain Arsenal	Brian Anderson	(303) 289-0120
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Fort Bliss, TX	(915) 568-2121
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Fort Dix, NJ	(609) 562-1011
Fort Hood, TX	(817) 287-1110
Fort Jackson, SC	(803) 751-7601
Fort Knox, KY	(502) 624-1181
Fort Leonard Wood, MO	(314) 367-0111
Fort Lewis, WA	(206) 967-1110
Fort McClellan, AL	(205) 848-4611
Fort Ord, CA	(408) 242-2211
Redstone Arsenal, AL	(205) 876-2151
Fort Riley, KS	(913) 239-3911
Fort Ruckers, AL	(205) 255-6181
Fort Sill, OK	(405) 321-2121
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Fort Leonard Wood, MO
Fort Knox, KY
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13. ABSTRACT (Maximum 200 words) <p>This document represents a research strategy to develop new and innovative technologies for treatment of heavy metal-contaminated soils on U.S. Army installations. For a technology to be considered, it must be effective, economically feasible, and available for implementation within 5 years. The activities undertaken to develop the research strategy are also described in this report.</p> <p>A survey of U.S. Army installations shows that soils contaminated by heavy metals are a common problem. Over 50 percent of the installations surveyed have potential heavy metal problems that may prove to be costly and/or beyond current technology to remediate. Of the six analytes found most often as contaminants in a U.S. Army Environmental Center (USAEC) database, five are classified as heavy metals. Chrome, lead, and cadmium are the most common metal contaminants. Further, the variety of contaminated media (e.g., water, soils, and structure) at military installations makes it likely that a variety of cleanup technologies will be required.</p> <p>The scientific basis of the interaction of heavy metals with different soils is briefly discussed in this report to provide an understanding of the efficacy of potential soil remediation techniques. Consideration is given to a 1987 review of soil remediation technologies produced by Roy F. Weston, Inc., for USAEC; to the results of the</p> <p style="text-align: right;">(Continued)</p>				
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deliberations of an advisory panel empaneled specifically to address metal/soil cleanup technologies; and to site visits and inquiries by personnel of the U.S. Army Engineer Waterways Experiment Station (WES) Environmental Laboratory.

Based upon these activities, researchers at WES have formulated a research strategy containing nine priority research efforts for treatment of soils contaminated with heavy metals. The objective and approach of each proposed research effort are discussed. A companion report ("Technology Assessment of Currently Available and Developmental Techniques for Heavy Metals-Contaminated Soils Treatment," Technical Report ILKP-93-4) updates and extends the 1987 Weston report by detailing 22 technologies having a reasonable potential for alleviating heavy metal soil contamination.